IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In Re Application of: § Atty File: CDT 1788 CON
PODREBARAC ET AL §
§
Serial No.: 10/820,399 § Group Art Unit: 1764
§
Filed: 04/07/2004 § Examiner: T. M. NGUYEN

For: PROCESS FOR THE SELECTIVE DESULFURIZATION OF
A MID RANGE GASOLINE CUT

BRIEF ON APPEAL

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

TABLE OF CONTENTS

I.
REAL PARTY IN INTEREST

The subject patent application is assigned of record to Catalytic Distillation

Technologies. Therefore, the real party in interest is Catalytic Distillation Technologies.

II.
RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences known to appellants or appellants' legal representative which will directly or indirectly affect or be affected by or have a bearing on the Board's decision in this appeal.

III.
STATUS OF CLAIMS

Claim 13 remains in the application. Claim 13 is on appeal. No claims are allowed.

IV.
STATUS OF AMENDMENTS

All amendments have been entered.

V.
SUMMARY OF THE CLAIMED SUBJECT MATTER

There is only one claim. There are no means plus functional or step plus function recitation under 35 USC 112, sixth paragraph recited in the claim.

The claimed subject matter of the claim on appeal is process for removal of sulfur from a full boiling range fluid cracked naphtha stream to meet higher standards for sulfur removal, by splitting the light portion of the stream utilizing a three-way naphtha splitter as a distillation column reactor to treat the lightest boiling range naphtha to remove the mercaptans contained therein by thioetherification and treating the components of the naphtha feed with the process that preserves the olefinic while most expediently removing the sulfur compounds. Mercaptans reacted with diolefins in the naphtha to form sulfides and are removed in that form. (Spec. page 4, lines 17-26).

Referring to the figure naphtha 101 and hydrogen 102 are feed to a distillation

column reactor 10. The light naphtha is boiled up into the catalyst in the rectification sections 11 and 12 where the mercaptans react with diolefins in the naphtha to form sulfides which are higher boiling and thus are separated out with the heavy naphtha (Spec. page 10, lines 18-21) as bottoms 104 (Spec. page 10, lines 30-31) and the light naphtha having reduced sulfur removed as overheads 103. (Spec. page 10, lines 24-25).

The mid-cut (intermediate naphtha) sidedraw 105 of a thiophene cut is taken from the first distillation column reactor 10 which is passed through a stripping column 20 and hence to a to a thiophene reactor 40 where the desired sulfur level is obtained. (Spec. page 11, lines 1-7).

VI.
GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

THE REJECTION OF CLAIM 13 AS BEING OBVIOUS UNDER 35 USC 103 (a) OVER HEARN ET AL U.S. 5,597,476 IN VIEW OF MCDANIEL U.S. 2003/0136706.

A copy of the references cited by the examiner and relied on in the final rejection are attached in (IX) EVIDENCE APPENDIX: U.S. 5,597,476 (Hearn et al) and U.S. 2003/0136706 (McDaniel et al).

McDaniel is prior art to the present application, which has an effective filing date of March 8, 2002, **only** because of the filing date of the provisional. Since the provisional is not publically available, applicants request that the examiner certify to the board and the applicants that there is literal support in the provisional for that which the examiner relies in the rejection.

VII.
ARGUMENT

GROUND: THE REJECTION OF CLAIM 13 AS BEING OBVIOUS UNDER 35 USC 103

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(a) OVER HEARN ET AL U.S. 5,597,476 IN VIEW OF MCDANIEL U.S. 2003/0136706.

There is only one claim.

Hearn feeds naphtha to a first distillation column reactor which acts as a depentanizer or dehexanizer with the lighter material containing most of the olefins and mercaptans being boiled up into a first distillation reaction zone where the mercaptans are reacted with diolefins to form sulfides which are removed in the bottoms along with any higher boiling sulfur compounds. The bottoms, which contain the sulfides, thiophenes and heavier mercaptan (see col. 2, lines 46-56; col. 3, lines 51-53; col. 4, lines 4-5, lines 41-43; col. 6, lines 62-64; col. 7, lines 6-20 and claims), are subjected to hydrodesulfurization in a second distillation column reactor where the sulfur compounds are converted to H_2S and removed. The lighter fraction containing most of the olefins is not subjected to the more harsh hydrogenation conditions of the second reactor. The point of Hearn is the removal of sulfur compounds, without reducing the olefin content of the feed.

Thus, in Hearn the stream containing the thiophenes are in the bottom stream, there is no suggestion in that reference that they be anywhere else.

In the present invention it was been found that the light FCC naphtha cut just below the light fraction also contains mercaptans and a significant amount of thiophenes. The mercaptans in this cut may be removed by the thioetherification, **but the thiophenes remain** and this cut will not meet sulfur requirements. (Spec. page 4, lines 7-10). The thioetherification carried out in the present process converts mercaptans to sulfides by the reaction with diolefins. The sulfides are heavy and are removed in the bottoms. The thiophenes in the present process do not react to form the heavy sulfides.

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Under § 103, the scope and content of the prior art are to be determined; the differences between the prior art and the claims at issue are to be ascertained; and the level of ordinary skill in the pertinent art resolved. Against this background, the obviousness or nonobviousness of the subject is determined. See Graham v. John Deere, 148 USPQ 459 (S. Ct. 1966).

The examiner notes that Hearn does not separate the naphtha into three fractions nor the further hydrodesulfurization of an intermediate fraction.

While it is true that McDaniel carries out a reaction of a hydrocarbon stream containing thiophenes then splits the product into at least three streams for further handling, it also true that the thiophenic compounds undergo conversion to the refractory sulfur compounds (para. 49) which are in the third fraction (paragraph 0051, line 5-9) which also contains the thiophenic compounds and which is subjected to the vigorous hydrodesulfurization (paragraph 0051 lines 10-end). Thus, McDaniel is treating essentially the same fraction as Hearn, i.e., the bottoms, with no suggestion in the references to do anything else. However, the reactions in Hearn is not the same as McDaniel since the thiophenic compounds react (are converted) in the McDaniel process. It is respectfully submitted that the combination of references, fails to make out a prima facie case of obviousness. Furthermore, there would appear to be no thiophenes in McDaniel's intermediate stream, hence the proposed rationale that it would be obvious to separate the Hearn product into 3 streams and to treat the intermediate stream, as McDaniel (the third or heavy stream) is rebutted by the facts that the intermediate stream of Hearn can be expected to contain thiophene, while the intermediate stream of McDaniel does not.

There would be no incentive to split Hearn's product into 3 streams based on

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McDaniel since as is taught by McDaniel, the refractory adducts and thiophenic compounds are being treated **in the bottom fraction**. It is not shown or remotely suggested by either reference that a thiophene cut should te separately removed and treated. The thiophenes would not require the strong hydrogenation of the refractory bottoms of either Hearn or McDaniel. Thus, the olefin content and the hence the octane rating of the overall streams will be greater by having the thiophene treated separately from the other bottoms.

Claim 13 is very clear that the thiophenes are in the intermediate fraction not the bottoms, which is removed and treated:

"(d) removing an intermediate naphtha as a side draw from said distillation column reactor containing thiophene, diolefins boiling in the range of thiophene and mercaptans boiling in the range of thiophene...

(f) feeding said intermediate naphtha to a single pass fixed bed reactor containing a hydrodesulfurization catalyst where substantially all of any remaining sulfides and other organic sulfur compounds are reacting with hydrogen to form hydrogen sulfide."

The examiner has urged that McDaniel's examples show the intermediate fraction contains thiophenes, but TABLE V is deceptive. In fact the examples are not consistent with the McDaniel disclosure. In paragraph 0138, McDaniel is at great pain to point out that the fractionation was less than ideal and if the fractionation had been carried ideally the sulfur level (which would include the thiophenes) would have been significantly lower in the overheads and the intermediate fraction (100-200°C). McDaniel points out the

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results of the test would have been significant if the fractionation had been more ideal. In other words the example is not in line with McDaniel's invention. In the invention the sulfur would have been in the bottoms, not in either the overheads or the intermediate fraction and the disclosures would not have provided any incentive for treating the intermediate fraction. It would be inappropriate to rely on that which the inventor of the reference teaches to be not the desired or expected result to achieve the objectives of the invention.

It is well settled that a rejection based on § 103 must rest upon a factual basis rather than conjure or speculation. "Where the legal conclusion of [of obviousness] is not supported by the facts it cannot stand." *In re Warner*, 379 F.2d 1011, 1017, 154 USPQ 173, 178 (CCPA 1967); see also *In re Sporck*, 301 F.2d 686, 690, 133 USPQ 360,364 (CCPA 1962). "Obviousness cannot be established by combining teachings of the prior art to produce the claimed invention, *absent* some teaching suggestion or incentive supporting the combination." *In re Geiger*, 2 USPQ2d 1276 (CAFC 1987). Hence, without the requisite teaching, suggestions or incentives there is no *prima facie* case and the rejection must fail. See also *In re Fine*, 5 USPQ2d 1596 and *Ex parte Levengood*, 28 USPQ2d 1300 (BdPatApp 1993). It is submitted that the total failure of either reference to express any interest in the thiophene cut, but rather to treat the thiophenes as just another component of the heavy fraction (and as detailed above McDaniel states the sulfur compounds **are** in the bottoms if the lab work had been carried out properly) fails to provide any incentive to rearrange and modify the two reference processes to arrive at the present claimed invention.

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than conjure or speculation. "Where the legal conclusion of [of obviousness] is not supported by the facts it cannot stand." *In re Warner*, 379 F.2d 1011, 1017, 154 USPQ 173, 178 (CCPA 1967); see also *In re Sporck*, 301 F.2d 686, 690, 133 USPQ 360,364 (CCPA 1962). "Obviousness cannot be established by combining teachings of the prior art to produce the claimed invention, *absent* some teaching suggestion or incentive supporting the combination." *In re Geiger*, 2 USPQ2d 1276 (CAFC 1987). Hence, without the requisite teaching, suggestions or incentives there is no *prima facie* case and the rejection must fail. The court was addressing piecemeal combination of teachings, which could be argued met the claims, however, there is no proposed combination, and thus does not even meet the claims of the present invention and does not even rise to the level of putative *prima facie* case. See also *In re Fine*, 5 USPQ2d 1596 and *Ex parte Levengood*, 28 USPQ2d 1300 (BdPatApp 1993).

The final determination is whether the combined disclosures put the invention in the possession of the public. See *Beckman Instruments, Inc. v. LKB Produkter AB*, 13 USPQ2d 1301 (Fed Cir. 1989) where the court held that "in order to render a claimed apparatus or method obvious, the prior art must enable one skilled in the art to make and use the apparatus or method."

The examiner has speculated that the apparent bulk density of the supports of either Frenzel et al or Brown et al must be within the claimed range because the disclosed materials are similar. Silence in a reference is not a proper substitute for an adequate disclosure of facts. See *In re Burt*, 148 USPQ 548 (CCPA 1966). Furthermore, mere speculation by the examiner is not a substitute of evidence. *In re Warner, supra.*
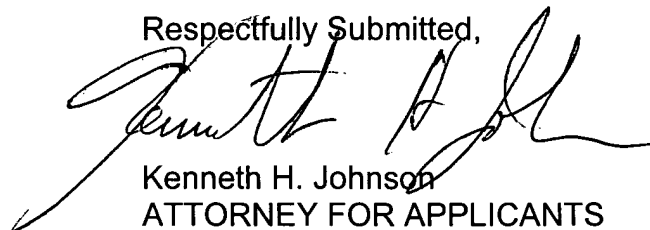
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Conclusion

It is submitted that the combinations of art as proposed by the examiner is based on the applicants' motivation to make the claimed invention rather than any suggestion in the references.

Applicants respectfully request that the board reverse the examiner.

Respectfully Submitted,

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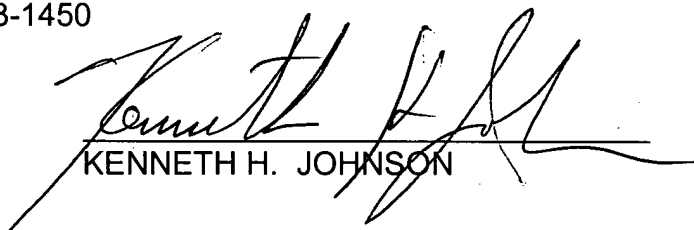Houston, Texas 77263
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Date 02/12/2007

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

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on 02/12/2007.

KENNETH H. JOHNSON

CLAIMS APPENDIX

13. A process for removal of sulfur from a full boiling range fluid cracked naphtha stream comprising the steps of:

(a) feeding hydrogen and a full boiling range naphtha feed containing olefins, diolefins, mercaptans, thiophene and other organic sulfur compounds to a distillation column reactor;

(b) concurrently in said distillation column reactor:

(i) reacting a portion of the mercaptans contained within said full boiling range naphtha stream with a portion of the diolefins contained within said full boiling range naphtha stream to produce sulfides and

(ii) separating said full boiling range naphtha stream into three fractions by fractional distillation;

(c) removing product from said distillation column reactor comprising a light naphtha containing substantially no mercaptans, sulfides or other organic sulfur compounds as an overheads;

(d) removing an intermediate naphtha as a side draw from said distillation column reactor containing thiophene, diolefins boiling in the range of thiophene and mercaptans boiling in the range of thiophene;

(e) removing a heavy naphtha from said distillation column reactor containing said sulfides and other organic sulfur compounds as a bottoms;

(f) feeding said intermediate naphtha to a single pass fixed bed reactor containing a hydrodesulfurization catalyst where substantially all of any remaining sulfides and other

organic sulfur compounds are reacting with hydrogen to form hydrogen sulfide.

IX.

EVIDENCE APPENDIX

A copy of each references cited by the examiner and relied on in the rejection:

U.S. 5,597,476 (Hearn et al)

U.S. 2003/0136706 (McDaniel et al)

[54] GASOLINE DESULFURIZATION PROCESS

[75] Inventors: **Dennis Hearn**, Pasadena; **Thomas P. Hickey**, Houston, both of Tex.

[73] Assignee: **Chemical Research & Licensing Company**, Pasadena, Tex.

[21] Appl. No.: **519,736**

[22] Filed: **Aug. 28, 1995**

[51] Int. Cl.^{6} **C10G 53/02**

[52] U.S. Cl. .... **208/208 R**; 208/209; 208/211; 208/347

[58] Field of Search .... 502/300; 208/208 R, 208/209, 211

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,671,603	6/1972	Hagemeyer et al.	260/677 A
4,055,483	10/1977	Mertzweiller et al.	208/213
4,123,502	10/1978	Hölter et al.	423/230
4,194,964	3/1980	Chen et al.	208/108
4,451,607	5/1984	Garcia et al.	524/494
4,486,297	12/1984	Matsumoto et al.	208/211
4,676,887	6/1987	Fischer et al.	208/61
4,690,806	9/1987	Schorfheide	423/230
4,827,076	5/1989	Kokayeff et al.	585/737
4,941,968	7/1990	Reid	208/236
4,990,242	2/1991	Louie et al.	208/218
5,073,236	12/1991	Gelbein et al.	203/29
5,154,817	10/1992	Reid	208/48 AA
5,266,546	11/1993	Hearn	502/300
5,290,427	3/1994	Fletcher et al.	208/89
5,320,742	6/1994	Fletcher et al.	208/89
5,321,163	6/1994	Hickey et al.	568/59
5,322,615	6/1994	Holtermann et al.	208/91
5,348,641	9/1994	Shih	208/89
5,431,888	7/1995	Hickey et al.	422/191
5,431,890	7/1995	Crossland et al.	422/211

Primary Examiner—Helane Myers
Attorney, Agent, or Firm—Kenneth H. Johnson

[57] **ABSTRACT**

A catalytic cracked naphtha is desulfurized with minimum loss of olefins and octane. The naphtha is fed to a first distillation column reactor which acts as a depentanizer or dehexanizer with the lighter material containing most of the olefins and mercaptans being boiled up into a first distillation reaction zone where the mercaptans are reacted with diolefins to form sulfides which are removed in the bottoms along with any higher boiling sulfur compounds. The bottoms are subjected to hydrodesulfurization in a second distillation column reactor where the sulfur compounds are converted to H$_2$S and removed. The lighter fraction containing most of the olefins is thus not subjected to the more harsh hydrogenation conditions of the second reactor.

13 Claims, 1 Drawing Sheet

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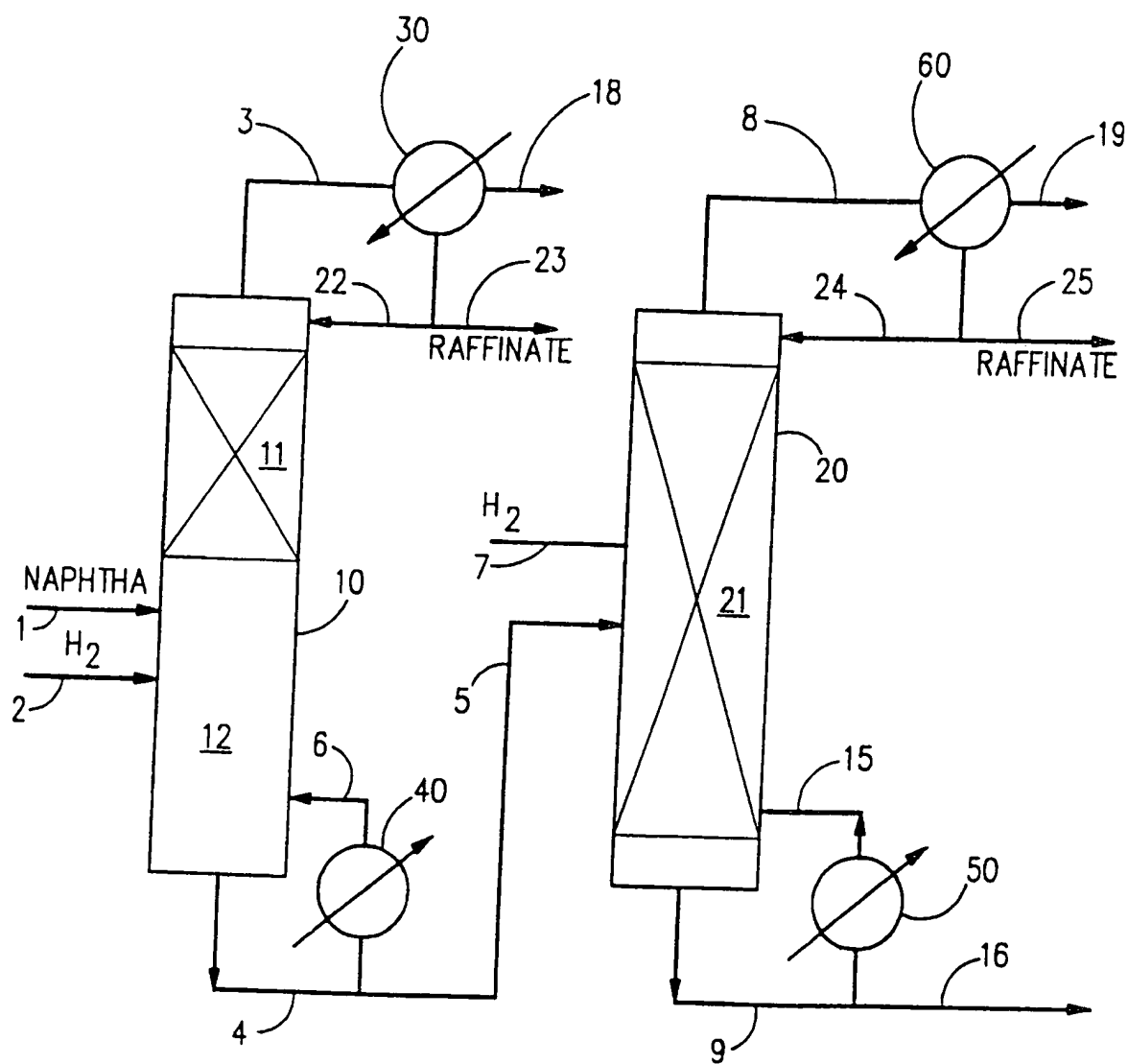[56] References Cited

U.S. PATENT DOCUMENTS

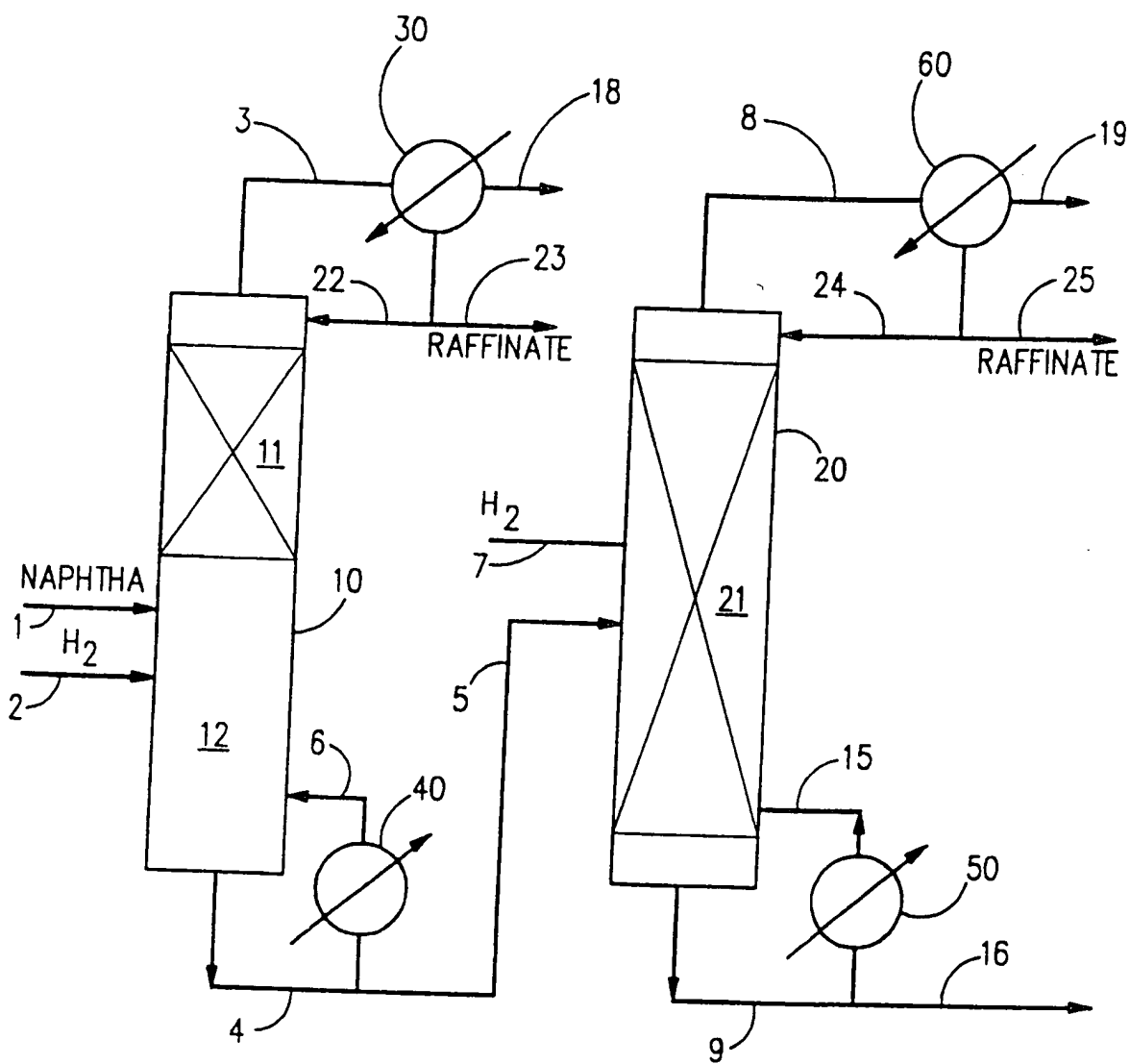|			
3,671,603	6/1972	Hagemeyer et al.	260/677 A
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A catalytic cracked naphtha is desulfurized with minimum loss of olefins and octane. The naphtha is fed to a first distillation column reactor which acts as a depentanizer or dehexanizer with the lighter material containing most of the olefins and mercaptans being boiled up into a first distillation reaction zone where the mercaptans are reacted with diolefins to form sulfides which are removed in the bottoms along with any higher boiling sulfur compounds. The bottoms are subjected to hydrodesulfurization in a second distillation column reactor where the sulfur compounds are converted to H_2S and removed. The lighter fraction containing most of the olefins is thus not subjected to the more harsh hydrogenation conditions of the second reactor.

13 Claims, 1 Drawing Sheet

GASOLINE DESULFURIZATION PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to a process for the removal of organic sulfur compounds from petroleum distillate streams. More particularly the invention involves a process to remove mercaptans, H₂S and other sulfur compounds from naphtha streams, by reacting the mercaptans and H₂S with diolefins in the streams to produce sulfides, which are removed along with the other sulfur compounds in a first reactive distillation column to a second reactive distillation column where the sulfur compounds are destructively hydrogenated.
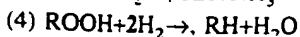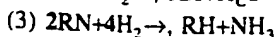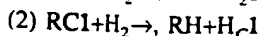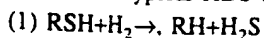
2. Related Information

Petroleum distillate streams contain a variety of organic chemical components. Generally the streams are defined by their boiling ranges which determine the compositions. The processing of the streams also affects the composition. For instance, products from either catalytic cracking or thermal cracking processes contain high concentrations of olefinic materials as well as saturated (alkanes) materials and poly-unsaturated materials (diolefins). Additionally, these components may be any of the various isomers of the compounds.

Cracked naphtha as it comes from the catalytic cracker has a relatively high octane number as a result of the olefins compounds contained therein. In some cases this fraction may contribute as much as half of the gasoline in the refinery pool together with a significant portion of the octane.

Catalytically cracked naphtha (gasoline boiling range material) currently forms a major part of the gasoline product pool in the United States and it provides a large portion of the sulfur. The sulfur impurities may require removal, usually by hydrotreating, in order to comply with product specifications or to ensure compliance with environmental regulations.

The most common method of removal of the sulfur compounds is by hydrodesulfurization (HDS) in which the petroleum distillate is passed over a solid particulate catalyst comprising a hydrogenation metal supported on an alumina base. Additionally copious quantities of hydrogen are included in the feed. The following equations illustrate the reactions in a typical HDS unit:

(1) $RSH + H_2 \rightarrow RH + H_2S$

(2) $RCl + H_2 \rightarrow RH + H_cl$

(3) $2RN + 4H_2 \rightarrow RH + NH_3$

(4) $ROOH + 2H_2 \rightarrow RH + H_2O$

Typical operating conditions for the HDS reactions are:

Temperature, °F.	600–780
Pressure, psig	600–3000
H₂ recycle rate, SCF/bbl	1500–3000
Fresh H₂ makeup, SCF/bbl	700–1000

After the hydrotreating is complete the product may be fractionated or simply flashed to release the hydrogen sulfide and collect the now sweetened naphtha. In addition to supplying high octane blending components the cracked naphthas are often used as sources of olefins in other processes such as etherifications. The conditions of

also saturate some of the olefinic compounds in the fraction reducing the octane and loss of source olefins.

Various proposals have been made for removing sulfur while retaining the more desirable olefins. Since the olefins in the cracked naphtha are mainly in the low boiling fraction of these naphthas and the sulfur containing impurities tend to be concentrated in the high boiling fraction the most common solution has been pre-fractionation prior to hydrotreating.

The predominant light or lower boiling sulfur compounds are mercaptans while the heavier or higher boiling compounds are thiophenes and other heterocyclic compounds. The separation by fractionation alone will not remove the mercaptans. However, in the past the mercaptans have been easily removed by oxidative processes such as Merox. A combination oxidative removal of the mercaptans followed by fractionation and hydrotreating of the heavier fraction is disclosed in U.S. Pat. No. 5,320,742. In the oxidative removal of the mercaptans the mercaptans are converted to the corresponding disulfides.

It is an advantage of the present invention that the sulfur is removed from the light olefin portion of the stream to a heavier portion of the stream without any substantial loss of olefins. All of the sulfur in the heavier portion is converted to H₂S by hydrodesulfurization and easily distilled away from the hydrocarbons.

SUMMARY OF THE INVENTION

Briefly the present invention is a process for removing sulfur from a naphtha boiling range hydrocarbon stream, comprising the steps of:

(a) feeding a naphtha boiling range hydrocarbon stream containing olefins, diolefins, mercaptans and thiophenes and an effectuating amount of hydrogen to a first distillation column reactor into a feed zone;

(b) boiling a fraction of said naphtha boiling range hydrocarbon stream containing mercaptans, diolefins and a substantial portion of said olefins upward into a first distillation reaction zone containing a Group VIII metal hydrogenation catalyst prepared in the form to act as a catalytic distillation structure under conditions to react a portion of said mercaptans with a portion of the diolefins to form sulfides and an overhead distillate product having a reduced mercaptan content;

(c) removing said sulfides, thiophenes and heavier mercaptans with a higher boiling fraction as bottoms from said first distillation column reactor;

(d) feeding said bottoms and hydrogen to a second distillation column reactor having a second distillation reaction zone containing a hydrodesulfurization catalyst prepared in the form to act as a catalytic distillation structure under conditions to react a portion of said sulfides, thiophenes and heavier mercaptans with said hydrogen to form H₂S;

(e) removing said H₂S as a gas from the overheads from said second distillation column reactor; and

(f) recovering a naphtha product from said second distillation column reactor. H₂S in the first reactor may react in a similar manner as the mercaptans to form sulfides with the diolefins under the same conditions.

BRIEF DESCRIPTION OF THE DRAWING

The figure is a flow diagram in schematic form of the

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GASOLINE DESULFURIZATION PROCESS

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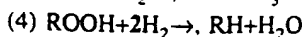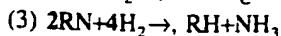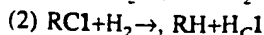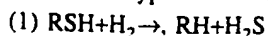
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Catalytically cracked naphtha (gasoline boiling range material) currently forms a major part of the gasoline product pool in the United States and it provides a large portion of the sulfur. The sulfur impurities may require removal, usually by hydrotreating, in order to comply with product specifications or to ensure compliance with environmental regulations.

The most common method of removal of the sulfur compounds is by hydrodesulfurization (HDS) in which the petroleum distillate is passed over a solid particulate catalyst comprising a hydrogenation metal supported on an alumina base. Additionally copious quantities of hydrogen are included in the feed. The following equations illustrate the reactions in a typical HDS unit:

(1) RSH+H$_2$→, RH+H$_2$S

(2) RC1+H$_2$→, RH+H$_c$1

(3) 2RN+4H$_2$→, RH+NH$_3$

(4) ROOH+2H$_2$→, RH+H$_2$O

Typical operating conditions for the HDS reactions are:

Temperature. °F.	600–780
Pressure. psig	600–3000
H$_2$ recycle rate. SCF/bbl	1500–3000
Fresh H$_2$ makeup, SCF/bbl	700–1000

After the hydrotreating is complete the product may be fractionated or simply flashed to release the hydrogen sulfide and collect the now sweetened naphtha. In addition to supplying high octane blending components the cracked naphthas are often used as sources of olefins in other processes such as etherifications. The conditions of

2

also saturate some of the olefinic compounds in the fraction reducing the octane and loss of source olefins.

Various proposals have been made for removing sulfur while retaining the more desirable olefins. Since the olefins in the cracked naphtha are mainly in the low boiling fraction of these naphthas and the sulfur containing impurities tend to be concentrated in the high boiling fraction the most common solution has been pre-fractionation prior to hydrotreating.

The predominant light or lower boiling sulfur compounds are mercaptans while the heavier or higher boiling compounds are thiophenes and other heterocyclic compounds. The separation by fractionation alone will not remove the mercaptans. However, in the past the mercaptans have been easily removed by oxidative processes such as Merox. A combination oxidative removal of the mercaptans followed by fractionation and hydrotreating of the heavier fraction is disclosed in U.S. Pat. No. 5,320,742. In the oxidative removal of the mercaptans the mercaptans are converted to the corresponding disulfides.

It is an advantage of the present invention that the sulfur is removed from the light olefin portion of the stream to a heavier portion of the stream without any substantial loss of olefins. All of the sulfur in the heavier portion is converted to H$_2$S by hydrodesulfurization and easily distilled away from the hydrocarbons.

SUMMARY OF THE INVENTION

Briefly the present invention is a process for removing sulfur from a naphtha boiling range hydrocarbon stream, comprising the steps of:

(a) feeding a naphtha boiling range hydrocarbon stream containing olefins, diolefins, mercaptans and thiophenes and an effectuating amount of hydrogen to a first distillation column reactor into a feed zone;

(b) boiling a fraction of said naphtha boiling range hydrocarbon stream containing mercaptans, diolefins and a substantial portion of said olefins upward into a first distillation reaction zone containing a Group VIII metal hydrogenation catalyst prepared in the form to act as a catalytic distillation structure under conditions to react a portion of said mercaptans with a portion of the diolefins to form sulfides and an overhead distillate product having a reduced mercaptan content;

(c) removing said sulfides, thiophenes and heavier mercaptans with a higher boiling fraction as bottoms from said first distillation column reactor;

(d) feeding said bottoms and hydrogen to a second distillation column reactor having a second distillation reaction zone containing a hydrodesulfurization catalyst prepared in the form to act as a catalytic distillation structure under conditions to react a portion of said sulfides, thiophenes and heavier mercaptans with said hydrogen to form H$_2$S;

(e) removing said H$_2$S as a gas from the overheads from said second distillation column reactor: and

(f) recovering a naphtha product from said second distillation column reactor. H$_2$S in the first reactor may react in a similar manner as the mercaptans to form sulfides with the diolefins under the same conditions.

BRIEF DESCRIPTION OF THE DRAWING

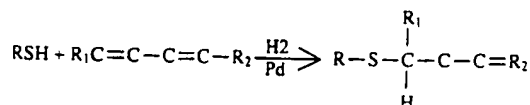The figure is a flow diagram in schematic form of the

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Typically cracked naphtha also contains diolefins which are not desirable because of their instability in storage.

The present process preferably operates in the first distillation column reactor at overhead pressure in the range between 0 and 250 psig and temperatures within said distillation reaction zone in the range of 100° F. to 300° F., preferably 130° F. to 270° F.

The feed and the hydrogen are preferably fed to the distillation column reactor separately or they may be mixed prior to feeding. A mixed feed is fed below the catalyst bed or at the lower end of the bed. Hydrogen alone is fed below the catalyst bed and the hydrocarbon stream is fed below the bed. The pressure selected is that which maintains catalyst bed temperature between 100° F. and 300° F.

Under these conditions in the first column diolefins react with the mercaptans and H_2S contained therein to form sulfides which can be separated from the lower boiling fraction containing most of the olefins. The equation of interest which describes the reaction is:

$$RSH + R_1C{=}C{-}C{=}C{-}R_2 \xrightarrow{\text{H2}} R{-}S{-}\overset{R_1}{\underset{H}{\overset{|}{\underset{|}{C}}}}{-}C{-}C{=}R_2$$

Where R, R_1 and R_2 are independently selected from hydrogen and hydrocarbyl groups of 1 to 20 carbon atoms. This may be compared to the HDS reaction of the second column which consumes hydrogen. The only hydrogen consumed in the removal of the mercaptans and/or hydrogen sulfide (H_2S) in the present invention is that necessary to keep the catalyst in the reduced "hydride" state. If there is concurrent hydrogenation of the dienes, then hydrogen will be consumed in that reaction.

The higher boiling fraction containing the sulfides reaction products and thiophenic and heterocyclic sulfur compounds are then hydrotreated generally at pressures in the range of 25 to less than about 300 psig and temperatures in the range of 400° F. to 700° F. to convert the organic sulfur compounds to H_2S which is removed by fractionation. The H_2S can be converted to elemental sulfur by conventional means known in the art.

In a first embodiment the full boiling range cracked naphtha is fed to a depentanizer which fractionates the C_5 and lighter boiling components from the remaining naphtha. Additionally the depentanizer contains a bed of suitable catalyst which acts as a distillation structure and also causes the diolefins within the naphtha to react with the mercaptans to form sulfides which are much higher boiling than the C_5 and lighter fraction. The sulfides are removed with the C_6+ bottoms which also contain the thiophenes and other heterocyclic sulfur compounds. The lighter C_5 fraction, containing the desirable olefins, is removed as overheads and contains essentially no sulfur compounds. Additionally the diolefins will also react with H_2S contained in the naphtha feed to form sulfides further sweetening the C_5 fraction.

The C_6+ fraction is fed to a second distillation column reactor where hydrogen is added to react the organic sulfur compounds with the hydrogen to form H_2S which can be removed by distillation. The use of a distillation column reactor which has liquid condensing within the reactor allows for much lower hydrogen partial pressure than previously used in standard hydrotreating.

Additionally the catalyst used also promotes isomeriza-tion of the olefins contained within the C_5 fraction which

In a second embodiment the first distillation column reactor is a dehexanizer rather than a depentanizer. The overheads will contain more of the naphtha and more of the olefin. The bottoms will still contain the sulfides, thiophenes and other heterocyclic organic sulfur compounds. The first embodiment is preferred when the overhead stream is used as a feed for tertiary amyl methyl ether (TAME) production or alkylation.

The feed to the process comprises a sulfur-containing petroleum fraction which boils in the gasoline boiling range. Feeds of this type include light naphthas having a boiling range of about C_5 to 330° F. and full range naphthas having a boiling range of C_5 to 420° F. Generally the process is useful on the naphtha boiling range material from catalytic cracker products because they contain the desired olefins and unwanted sulfur compounds. Straight run naphthas have very little olefinic material, and unless the crude source is "sour", very little sulfur.

The sulfur content of the catalytically cracked fractions will depend upon the sulfur content of the feed to the cracker as well as the boiling range of the selected fraction used as feed to the process. Lighter fractions will have lower sulfur contents than higher boiling fractions. The front end of the naphtha contains most of the high octane olefins but relatively little of the sulfur. The sulfur components in the front end are mainly mercaptans and typical of those compounds are: methyl mercaptan (b.p. 43° F.), ethyl mercaptan (b.p. 99° F.), n-propyl mercaptan (b.p. 154° F.), iso-propyl mercaptan (b.p. 135–140° F.), iso-butyl mercaptan (b.p. 190° F.), tert-butyl mercaptan (b.p. 47° F.), n-butyl mercaptan (b.p. 208° F.), sec-butyl mercaptan (b.p. 203° F.), iso-amyl mercaptan (b.p. 250° F.), n-amyl mercaptan (b.p. 259° F.), α-methylbutyl mercaptan (b.p. 234° F.), α-ethylpropyl mercaptan (b.p. 293° F.), n-hexyl mercaptan (b.p. 304° F.), 2-mercapto hexane (b.p. 284° F.), and 3-mercapto hexane (b.p. 135° F.).

Typical diolefins in the C_5 boiling range fraction include: isoprene (2-methyl butadiene-1,3), cis and trans piperylenes (cis and trans 1,3-pentadienes), and minor amounts of buta-dienes.

Typical sulfur compounds found in the heavier boiling fraction include the heavier mercaptans, thiophenes sulfides and disulfides.

Catalysts which are useful in either of the reactions utilized in the invention include the Group VIII- metals. Generally the metals are deposited as the oxides on an alumina support. In the first column the catalysts are characterized as hydrogenation catalysts. The reaction of the diolefins with the sulfur compounds is selective over the reaction of hydrogen with olefinic bonds. The preferred catalysts are palladium and/or nickel or dual bed as shown in copending U.S. patent application Ser. No. 08/500,101 filed Jul. 10, 1995, which is incorporated herein by reference, since in this column the sulfur removal is carried out with the intention to preserve the olefins. Although the metals are normally deposited as oxides, other forms may be used. The nickel is believed to be in the sulfide form during the hydrogenation.

In the second column, it is the purpose to destroy the sulfur compounds to produce a hydrocarbon stream containing H_2S which is easily separated from the heavier components therein. Without the concern for the olefins, and the necessity to carry out a destructive hydrogenation of the sulfides and other sulfur compounds in this column, hydrodesulfurization catalyst comprising two metal oxides
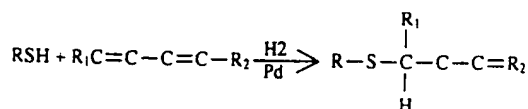
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The C$_6$+ fraction is fed to a second distillation column reactor where hydrogen is added to react the organic sulfur compounds with the hydrogen to form H$_2$S which can be removed by distillation. The use of a distillation column reactor which has liquid condensing within the reactor allows for much lower hydrogen partial pressure than previously used in standard hydrotreating.

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Catalysts which are useful in either of the reactions utilized in the invention include the Group VIII metals. Generally the metals are deposited as the oxides on an alumina support. In the first column the catalysts are characterized as hydrogenation catalysts. The reaction of the diolefins with the sulfur compounds is selective over the reaction of hydrogen with olefinic bonds. The preferred catalysts are palladium and/or nickel or dual bed as shown in copending U.S. patent application Ser. No. 08/500,101 filed Jul. 10, 1995, which is incorporated herein by reference, since in this column the sulfur removal is carried out with the intention to preserve the olefins. Although the metals are normally deposited as oxides, other forms may be used. The nickel is believed to be in the sulfide form during the hydrogenation.

In the second column, it is the purpose to destroy the sulfur compounds to produce a hydrocarbon stream containing H$_2$S which is easily separated from the heavier components therein. Without the concern for the olefins, and the necessity to carry out a destructive hydrogenation of the sulfides and other sulfur compounds in this column, hydrodesulfurization catalyst comprising two metal oxides

tungsten and mixtures thereof are preferred. More preferably cobalt modified with nickel. molybdenum, tungsten and mixtures thereof are the preferred catalyst.

The catalysts may be supported. The supports are usually small diameter extrudates or spheres. The catalyst must then be prepared in the form of a catalytic distillation structure. The catalytic distillation structure must be able to function as catalyst and as mass transfer medium. The catalyst must be suitably supported and spaced within the column to act as a catalytic distillation structure. In a preferred embodiment the catalyst is contained in a woven wire mesh structure as disclosed in U.S. Pat. No 5,266,546, which is hereby incorporated by reference. Other catalytic distillation structures useful for this purpose are disclosed in U.S. Pat. No. 4,731,229, 5,073,236 and 5,431,890 which are also incorporated by reference.

A suitable catalyst for the reaction of the diolefins with the mercaptans is 0.4 wt % Pd on 7 to 14 mesh Al_2O_3 (alumina) spheres, supplied by United Catalysts Inc., designated as G-68C. Typical physical and chemical properties of the catalyst as provided by the manufacturer are as follows:

TABLE I

Designation	G-68C
Form	Sphere
Nominal size	7 × 14 mesh
Pd. wt %	0.4 (0.37–0.43)
Support	High purity alumina

Another catalyst useful for the mercaptan-diolefin reaction is 58 wt % Ni on 8 to 14 mesh alumina spheres, supplied by Calcicat, designated as E-475-SR. Typical physical and chemical properties of the catalyst as provided by the manufacturer are as follows:

TABLE II

Designation	E-475-SR
Form	Spheres
Nominal size	8 × 14 Mesh
Ni wt %	54
Support	Alumina

The hydrogen rate to the reactor must be sufficient to maintain the reaction, but kept below that which would cause flooding of the column which is understood to be the "effectuating amount of hydrogen" as that term is used herein. Generally in the first column the mole ratio of hydrogen to diolefins and acetylenes in the feed is at least 1.0 to 1.0 and preferably 2.0 to 1.0. In the second reactor column larger quantities of hydrogen are preferably present to convert all of the sulfur compounds to H_2S. Based on the sulfur in the feed to the second column reactor the mole ratio of H_2:S is in the range of 10 to 1000:1

The catalyst also catalyzes the selective hydrogenation of the polyolefins contained within the light cracked naphtha and to a lesser degree the isomerization of some of the mono-olefins. Generally the relative rates of reaction for various compounds are in the order of from faster to slower:

(1) reaction of diolefins with mercaptans

(2) hydrogenation of diolefins

(3) isomerization of the mono-olefins

(4) hydrogenation of the mono-olefins.

Catalysts suitable for the hyrodesulfurization reaction include cobalt-molybdenum. nickel-molybdenum and nickel-tungsten. The metals are generally present as oxides supported on a neutral base such as alumina, silica-alumina

or prior to use by exposure to sulfur compound containing streams. The properties of a typical hydrodesulfurization catalyst in Table III below.

TABLE III

Manufacture	Criterion	Criterion
Designation	C-448	C-411SM3
Form	Trilobe	Extrudate
Nominal size	1.2 mm	1.2 mm
Metal, Wt %		
Cobalt	2–5%	—
Molybdenum	5–20%	21.5%
Nickel	—	3.5%
Support	alumina	alumina

A typical charge to the process is a full range naphtha from a fluid catalytic cracking unit. The properties of such a naphtha is shown in Table IV below:

TABLE IV

ASTM boiling range, °F.	80–420
Total Sulfur, wppm	1000–3000
Mercaptan Sulfur, wppm	10–200
Diolefins, wt %	0.3–1.0
Octane, RON/MON	87/84

In the first distillation column reactor the pressure is maintained at about 0 to 250 psig with the corresponding temperature in the distillation reaction zone of between 130° F. to 270° F. Hydrogen partial pressures of 0.1 to 70 psia, more preferably 0.1 to 10 are used, with hydrogen partial pressures in the range of 0.5 to 50 psia giving optimum results.

Surprisingly, in the second column a low total pressure in the range of 25 to less than 300 psig is required for the hydrodesulfurization and hydrogen partial pressure of less than 150 psi, preferably down to 0.1 psi can be employed preferably about 15 to 50 psi. The temperature in the distillation reaction zone is between 400° F. to 750° F. Hydrogen for the second distillation column reactor is fed in the range of one to ten standard cubic feet (SCF) per pound of feed. Nominal liquid hourly space velocities (liquid volume of feed per unit volume of catalyst) in the second column are in the range of 2–5.

Referring now to the figure a flow diagram in schematic form is shown to illustrate one embodiment of the invention. The naphtha is fed to a first distillation column reactor 10 via flow line 1 and an effectuating amount of hydrogen for the diolefin/mercaptan reaction is fed via flow line 2. Distillation column reactor 10 contains distillation reaction zone 11 in the upper end which contains the supported palladium catalyst for the diolefin/mercaptan reaction. As desired the column 10 may be run to take a C_5 and lighter or a C_6 and lighter as overheads. In either case the lighter fraction containing most of the octane improving olefins and the mercaptans is boiled up into the distillation reaction zone 11. In distillation reaction zone 11 substantially all of the mercaptans react with the diolefins to form higher boiling sulfides. The lower section of the first distillation column reactor 10 acts as a stripping section to separate the C_6+ or C_7+material from the lighter components. The diolefins formed in the distillation reaction zone 11 are also separated from the lighter fraction. The C_6+ or C_7+ material. containing the sulfides and the heavier thiophene type compounds are taken from the distillation column reactor 10 as bottoms via flow line 4. A reboiler 40 and reboiler return 6 are

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and condensed in overhead condenser 30. Product is taken via flow line 18 either to gasoline blending or further processing as desired. A reflux 22 is included for better reaction and separation. Raffinate product is taken via line 23.

The bottoms from the first distillation column reactor 10 is fed to second distillation column reactor 20 via flow line 5 and additional hydrogen for the hydrodesulfurization reaction is fed via flow line 7. The second distillation column reactor 20 contains a second distillation reaction zone 21 containing the cobalt/molybdenum catalyst for desulfurization. In second distillation reaction zone 21 the organic sulfur compounds (sulfides and thiophenes) react with hydrogen to form H₂S which is taken along with the overheads via flow line 8 and which can be easily separated from the overhead naphtha product by condensation of the naphtha. If necessary an H₂S stripping column may be added for the overhead product. Again a reflux 24 is used for better reaction and separation with raffinate product taken via line 25.

The bottoms is taken via flow line 9 and is substantially reduced in sulfur content as is the overheads and both may used as gasoline blending components. Product is taken via flow line 16 and a reboiler 50 is added for heat balance to the column 20. One of the benefits of the distillation column reactor for hydrodesulfurization is that some isomerization of the heavier olefin compounds occurs which almost makes up for the loss in octane due to monoolefin saturation.

EXAMPLE

A full range FCC naphtha having the characteristics noted above is fed to a three inch diameter distillation column reactor having a supported palladium catalyst in the upper 20 feet as a catalytic distillation structure and 10 feet of supported nickel catalyst below the palladium catalyst, both prepared as distillation structures in the manner disclosed in U.S. patent application Ser. No. 08/500,101 filed Jul. 10, 1995. The column is operated as a depentanizer to take a C₅ and lighter stream overhead. The bottoms from first column is fed to a second distillation column reactor which is a three inch diameter column having 30 feet of cobalt/molybdenum catalyst as a distillation structure. The column was operated to take a 350 ° F. overhead cut and the remainder as bottoms. Conditions and results are shown in TABLE V.

TABLE V

Run Number Hours on line	4057C5H2 166	1027HDS 308
First Column		
Feed Rate lbs/hr	347	
Total Sulfur, wppm	999	
Ethyl mercaptan, wppm	11	
Overhead, lbs/hr	39.3	
Total Sulfur, wppm	40	
Mercaptans, wppm	0	
Bottoms, lbs/hr	307.7	
Total Sulfur, wppm	1150	
Catalyst temperature, °F.		
Top	260	
Bottom	280	
Pressure, psig	100	
Hydrogen, SCFH	19	
H₂ partial press, psig	3.8	
Second Column		
Feed Rate lbs/hr		

TABLE V-continued

Run Number Hours on line	4057C5H2 166	1027HDS 308
Total Sulfur, wppm		1300
Overhead, lbs/hr		16
Total Sulfur, wppm	122	
Bottoms, lbs/hr		4
Total Sulfur, wppm		35
Catalyst temperature, °F.		
Top		552
Bottom		696
Pressure, psig		200
Hydrogen, SCFH		120
H₂ partial press, psig		75.5
Sulfur conversion,		92

The invention claimed is:

1. A process for removing sulfur from a naphtha boiling range hydrocarbon stream, comprising the steps of:
   (a) feeding a naphtha boiling range hydrocarbon stream containing olefins, diolefins, mercaptans and thiophenes and an effectuating amount of hydrogen to a first distillation column reactor into a feed zone;
   (b) boiling a fraction of said naphtha boiling range hydrocarbon stream containing mercaptans, diolefins and a substantial portion of said olefins upward into a first distillation reaction zone containing a Group VIII metal hydrogenation catalyst suitably supported and spaced in said first distillation column to act as a catalytic distillation structure under conditions to react a portion of said mercaptans with a portion of the diolefins to form sulfides and an overhead distillate product having a reduced mercaptan content;
   (c) removing said sulfides, thiophenes and heavier mercaptans with a higher boiling fraction as bottoms from said first distillation column reactor;
   (d) feeding said bottoms and hydrogen to a second distillation column reactor having a second distillation reaction zone containing a hydrodesulfurization catalyst suitably supported and spaced in said second distillation column to act as a catalytic distillation structure under conditions to react a portion of said sulfides, thiophenes and heavier mercaptans with said hydrogen to form H₂S;
   (e) removing said H₂S as a gas from the overheads from said second distillation column reactor; and
   (f) recovering a naphtha product from said second distillation column reactor.

2. The process according to claim 1 wherein said first distillation column reactor is a depentanizer and said overheads contain a C₅ and lighter fraction.

3. The process according to claim 1 wherein said first distillation column reactor is a dehexanizer and said overheads contain a C₆ and lighter fraction.

4. The process according to claim 1 wherein all of the liquid product from both distillation column reactors is combined for a gasoline blending component.

5. The process according to claim 1 wherein a first portion of the olefins contained within said bottoms is hydrogenated to alkanes and a second portion of the olefins contained within said bottoms is isomerized to produce a naphtha product from said second distillation column reactor having only a slightly reduced octane number.

6. The process according to claim 1 wherein said

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and condensed in overhead condenser **30**. Product is taken via flow line **18** either to gasoline blending or further processing as desired. A reflux **22** is included for better reaction and separation. Raffinate product is taken via line **23**.

The bottoms from the first distillation column reactor **10** is fed to second distillation column reactor **20** via flow line **5** and additional hydrogen for the hydrodesulfurization reaction is fed via flow line **7**. The second distillation column reactor **20** contains a second distillation reaction zone **21** containing the cobalt/molybdenum catalyst for desulfurization. In second distillation reaction zone **21** the organic sulfur compounds (sulfides and thiophenes) react with hydrogen to form H_2S which is taken along with the overheads via flow line **8** and which can be easily separated from the overhead naphtha product by condensation of the naphtha. If necessary an H_2S stripping column may be added for the overhead product. Again a reflux **24** is used for better reaction and separation with raffinate product taken via line **25**.

The bottoms is taken via flow line **9** and is substantially reduced in sulfur content as is the overheads and both may used as gasoline blending components. Product is taken via flow line **16** and a reboiler **50** is added for heat balance to the column **20**. One of the benefits of the distillation column reactor for hydrodesulfurization is that some isomerization of the heavier olefin compounds occurs which almost makes up for the loss in octane due to monoolefin saturation.

EXAMPLE

A full range FCC naphtha having the characteristics noted above is fed to a three inch diameter distillation column reactor having a supported palladium catalyst in the upper 20 feet as a catalytic distillation structure and 10 feet of supported nickel catalyst below the palladium catalyst, both prepared as distillation structures in the manner disclosed in U.S. patent application Ser. No. 08/500,101 filed Jul. 10, 1995. The column is operated as a depentanizer to take a C_5 and lighter stream overhead. The bottoms from first column is fed to a second distillation column reactor which is a three inch diameter column having 30 feet of cobalt/molybdenum catalyst as a distillation structure. The column was operated to take a 350° F. overhead cut and the remainder as bottoms. Conditions and results are shown in TABLE V.

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Total Sulfur, wppm	1150	
Catalyst temperature, °F.		
Top	260	
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Pressure, psig	100	
Hydrogen, SCFH	19	
H_2 partial press, psig	3.8	
Second Column		
Feed Rate lbs/hr		

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TABLE V-continued

Run Number	4057C5H2	1027HDS
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Total Sulfur, wppm		1300
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Catalyst temperature, °F.		
Top		552
Bottom		696
Pressure, psig		200
Hydrogen, SCFH		120
H_2 partial press, psig		75.5
Sulfur conversion,		92

The invention claimed is:

1. A process for removing sulfur from a naphtha boiling range hydrocarbon stream, comprising the steps of:

(a) feeding a naphtha boiling range hydrocarbon stream containing olefins, diolefins, mercaptans and thiophenes and an effectuating amount of hydrogen to a first distillation column reactor into a feed zone;

(b) boiling a fraction of said naphtha boiling range hydrocarbon stream containing mercaptans, diolefins and a substantial portion of said olefins upward into a first distillation reaction zone containing a Group VIII metal hydrogenation catalyst suitably supported and spaced in said first distillation column to act as a catalytic distillation structure under conditions to react a portion of said mercaptans with a portion of the diolefins to form sulfides and an overhead distillate product having a reduced mercaptan content;

(c) removing said sulfides, thiophenes and heavier mercaptans with a higher boiling fraction as bottoms from said first distillation column reactor;

(d) feeding said bottoms and hydrogen to a second distillation column reactor having a second distillation reaction zone containing a hydrodesulfurization catalyst suitably supported and spaced in said second distillation column to act as a catalytic distillation structure under conditions to react a portion of said sulfides, thiophenes and heavier mercaptans with said hydrogen to form H_2S;

(e) removing said H_2S as a gas from the overheads from said second distillation column reactor; and

(f) recovering a naphtha product from said second distillation column reactor.

2. The process according to claim 1 wherein said first distillation column reactor is a depentanizer and said overheads contain a C_5 and lighter fraction.

3. The process according to claim 1 wherein said first distillation column reactor is a dehexanizer and said overheads contain a C_6 and lighter fraction.

4. The process according to claim 1 wherein all of the liquid product from both distillation column reactors is combined for a gasoline blending component.

5. The process according to claim 1 wherein a first portion of the olefins contained within said bottoms is hydrogenated to alkanes and a second portion of the olefins contained within said bottoms is isomerized to produce a naphtha product from said second distillation column reactor having only a slightly reduced octane number.

6. The process according to claim 1 wherein said

from the group consisting of molybdenum, cobalt, nickel, tungsten and mixtures thereof.

7. The process according to claim 1 wherein the total pressure in said first distillation column reactor is in the range of 0 to 250 psig and the total pressure in said second distillation column reactor is in the range of 25 to less than 300 psig.

8. The process according to claim 7 wherein the hydrogen partial pressure in said second distillation column reactor is between 0.1 and 150 psi.

9. The process according to claim 1 wherein the temperature within said first distillation reaction zone is in the range of 230° F. to 270° F. and the temperature within said second distillation reaction zone is in the range of 400 ° F. to 750 ° F.

10. The process according to claim 1 further comprising removing an overhead stream from said second distillation column reactor and stripping the H_2S from said overhead stream.

11. The process according to claim 1 wherein the hydrogen flow rate to said second distillation column reactor is in the range of one to ten standard cubic feet per pound of feed to said second distillation column reactor.

12. The process according to claim 1 wherein said first supported catalyst comprises palladium oxide.

13. The process according to claim 1 wherein said first supported catalyst comprises nickel sulfide.

* * * * *

from the group consisting of molybdenum, cobalt, nickel, tungsten and mixtures thereof.

7. The process according to claim 1 wherein the total pressure in said first distillation column reactor is in the range of 0 to 250 psig and the total pressure in said second distillation column reactor is in the range of 25 to less than 300 psig.

8. The process according to claim 7 wherein the hydrogen partial pressure in said second distillation column reactor is between 0.1 and 150 psi.

9. The process according to claim 1 wherein the temperature within said first distillation reaction zone is in the range of 230° F. to 270° F. and the temperature within said second distillation reaction zone is in the range of 400° F. to 750° F.

10. The process according to claim 1 further comprising removing an overhead stream from said second distillation column reactor and stripping the H_2S from said overhead stream.

11. The process according to claim 1 wherein the hydrogen flow rate to said second distillation column reactor is in the range of one to ten standard cubic feet per pound of feed to said second distillation column reactor.

12. The process according to claim 1 wherein said first supported catalyst comprises palladium oxide.

13. The process according to claim 1 wherein said first supported catalyst comprises nickel sulfide.

* * * * *

(54) **SULFUR REMOVAL PROCESS**

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(57) **ABSTRACT**

A product of reduced sulfur content is produced from an olefin-containing hydrocarbon feedstock which includes sulfur-containing impurities. The feedstock is contacted with an olefin-modification catalyst in a reaction zone under conditions which are effective to produce an intermediate product which has a reduced amount of olefinic unsaturation relative to that of the feedstock as measured by bromine number. The intermediate product is then separated into at least three fractions of different volatility, and the lowest boiling first fraction is contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of its sulfur-containing impurities to hydrogen sulfide. The intermediate boiling fraction is contacted with a selective hydrotreating catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of its sulfur-containing impurities to hydrogen sulfide.
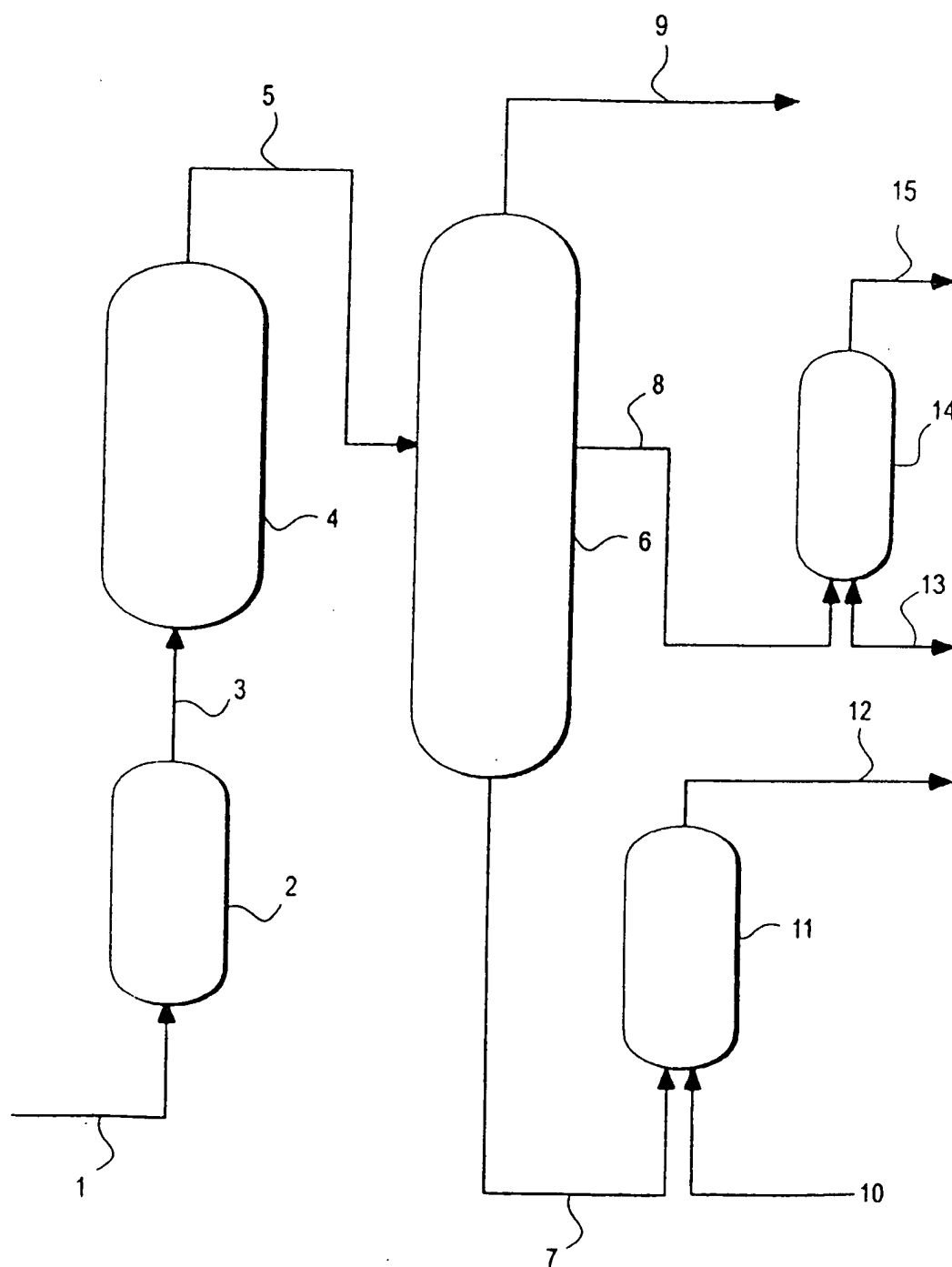
SULFUR REMOVAL PROCESS

[0001] The present application claims the benefit of U.S. provisional application No. 60/334,640 filed on Oct. 25, 2001.

FIELD OF THE INVENTION

[0002] This invention relates to a process for removing sulfur-containing impurities from olefin-containing hydrocarbon mixtures. More particularly, the process involves converting the feedstock to an intermediate product of reduced bromine number, separating the intermediate product into fractions of different boiling point, and subjecting the high boiling fraction to hydrodesulfurization, and the intermediate boiling fraction to selective hydrotreating.

BACKGROUND OF THE INVENTION

[0003] The fluidized catalytic cracking process is one of the major refining processes which is currently employed in the conversion of petroleum to desirable fuels such as gasoline and diesel fuel. In this process, a high molecular weight hydrocarbon feedstock is converted to lower molecular weight products through contact with hot, finely-divided, solid catalyst particles in a fluidized or dispersed state. Suitable hydrocarbon feedstocks typically boil within the range from about 205° C. to about 650° C., and they are usually contacted with the catalyst at temperatures in the range from about 450° C. to about 650° C. Suitable feedstocks include various mineral oil fractions such as light gas oils, heavy gas oils, wide-cut gas oils, vacuum gas oils, kerosenes, decanted oils, residual fractions, reduced crude oils and cycle oils which are derived from any of these as well as fractions derived from shale oils, tar sands processing, and coal liquefaction. Products from a fluidized catalytic cracking process are typically based on boiling point and include light naphtha (boiling between about 10° C. and about 221° C.), heavy naphtha (boiling between about 10° C. and about 249° C.), kerosene (boiling between about 180° C. and about 300° C.), light cycle oil (boiling between about 221° C. and about 345° C.), and heavy cycle oil (boiling at temperatures higher than about 345° C.).

[0004] Naphtha from a catalytic cracking process comprises a complex blend of hydrocarbons which includes paraffins (also known as alkanes), cycloparaffins (also known as cycloalkanes or naphthenes), olefins (as used herein, the term olefin includes all acyclic and cyclic hydrocarbons which contain at least one double bond and are not aromatic), and aromatic compounds. Such a material typically contains a relatively high olefin content and includes significant amounts of sulfur-containing aromatic compounds, such as thiophenic and benzothiophenic compounds, as impurities. For example, a light naphtha from the fluidized catalytic cracking of a petroleum derived gas oil can contain up to about 60 wt. % of olefins and up to about 0.7 wt. % of sulfur wherein most of the sulfur will be in the form of thiophenic and benzothiophenic compounds. However, a typical naphtha from the catalytic cracking process will usually contain from about 5 wt. % to about 40 wt. % olefins and from about 0.07 wt. % to about 0.5 wt. % sulfur.

[0005] Not only does the fluidized catalytic cracking process provide a significant part of the gasoline pool in the United States, it also provides a large proportion of the sulfur that appears in this pool. The sulfur in the liquid products

from this process is in the form of organic sulfur compounds and is an undesirable impurity which is converted to sulfur oxides when these products are utilized as a fuel. The sulfur oxides are objectionable air pollutants. In addition, they can deactivate many of the catalysts that have been developed for the catalytic converters which are used on automobiles to catalyze the conversion of harmful engine exhaust emissions to gases which are less objectionable. Accordingly, it is desirable to reduce the sulfur content of catalytic cracking products to the lowest possible levels.

[0006] Low sulfur products are conventionally obtained from the catalytic cracking process by hydrotreating either the feedstock to the process or the products from the process. The hydrotreating process involves treatment of the feedstock with hydrogen in the presence of a catalyst and results in the conversion of the sulfur in the sulfur-containing impurities to hydrogen sulfide, which can be separated and converted to elemental sulfur. The hydrotreating process can result in the destruction of olefins in the feedstock by converting them to saturated hydrocarbons through hydrogenation. This destruction of olefins by hydrogenation is usually undesirable because: (1) it results in the consumption of expensive hydrogen, and (2) the olefins are usually valuable as high octane components of gasoline. As an example, a typical naphtha of gasoline boiling range from a catalytic cracking process has a relatively high octane number as a result of a large olefin content. Hydrotreating such a material causes a reduction in the olefin content in addition to the desired desulfurization, and the octane number of the hydrotreated product decreases as the degree or severity of the desulfurization increases.

[0007] U.S. Pat. No. 5,865,988 (Collins et al.) is directed to a two step process for the production of low sulfur gasoline from an olefinic, cracked, sulfur-containing naphtha. The process involves: (a) passing the naphtha over a shape selective acidic catalyst, such as ZSM-5 zeolite, to selectively crack low octane paraffins and to convert some of the olefins and naphthenes to aromatics and aromatic side chains; and (2) hydrodesulfurizing the resulting product over a hydrotreating catalyst in the presence of hydrogen. It is disclosed that the initial treatment with the shape selective acidic catalyst removes the olefins which would otherwise be saturated in the hydrodesulfurization step.

[0008] International Patent Application No. WO 98/30655 (Huff et al.), published under the Patent Cooperation Treaty, discloses a process for the production of a product of reduced sulfur content from a feedstock wherein the feedstock is comprised of a mixture of hydrocarbons and contains organic sulfur compounds as unwanted impurities. This process involves converting at least a portion of the sulfur-containing impurities to sulfur-containing products of a higher boiling point by treatment with an alkylating agent in the presence of an acid catalyst and removing at least a portion of these higher boiling products by fractionation on the basis of boiling point.

[0009] U.S. Pat. Nos. 5,298,150 (Fletcher et al.); 5,346,609 (Fletcher et al.); 5,391,288 (Collins et al.); and 5,409,596 (Fletcher et al.) are all directed to a two step process for the preparation of a low sulfur gasoline wherein a naphtha feedstock is subjected to hydrodesulfurization followed by treatment with a shape selective catalyst to restore the octane which is lost during the hydrodesulfurization step.

[0010] U.S. Pat. No. 5,171,916 (Le et al.) is directed to a process for upgrading a light cycle oil by: (1) alkylating the heteroatom containing aromatics of the cycle oil with an aliphatic hydrocarbon having at least one olefinic double bond through the use of a crystalline metallosilicate catalyst; and (2) separating the high boiling alkylation product by fractional distillation. It is disclosed that the unconverted light cycle oil has a reduced sulfur and nitrogen content, and the high boiling alkylation product is useful as a synthetic alkylated aromatic functional fluid base stock.

[0011] U.S. Pat. No. 5,599,441 (Collins et al.) discloses a process for removing thiophenic sulfur compounds from a cracked naphtha by: (1) contacting the naphtha with an acid catalyst in an alkylation zone to alkylate the thiophenic compounds using the olefins present in the naphtha as an alkylating agent; (2) removing an effluent stream from the alkylation zone; and (3) separating the alkylated thiophenic compounds from the alkylation zone effluent stream by fractional distillation. It is also disclosed that the sulfur-rich high boiling fraction from the fractional distillation may be desulfurized using conventional hydrotreating or other desulfurization processes.

[0012] U.S. Pat. No. 5,863,419 (Huff, Jr. et al.) discloses a catalytic distillation process for the production of a product of reduced sulfur content from a feedstock wherein the feedstock is comprised of a mixture of hydrocarbons which contains organic sulfur compounds as unwanted impurities. The process involves carrying out the following process steps simultaneously within a distillation column reactor: (1) converting at least a portion of the sulfur-containing impurities to sulfur-containing products of a higher boiling point by treatment with an alkylating agent in the presence of an acid catalyst; and (2) removing at least a portion of these higher boiling products by fractional distillation. It is also disclosed that the sulfur-rich high boiling fraction can be efficiently hydrotreated at relatively low cost because of its reduced volume relative to that of the original feedstock.

[0013] More recently, U.S. Pat. No. 6,024,865 in the name of Bruce D. Alexander, George A. Huff, Vivek R. Pradhan, William J. Reagan and Roger H. Cayton disclosed a product of reduced sulfur content which is produced from a feedstock which is comprised of a mixture of hydrocarbons and includes sulfur-containing aromatic compounds as unwanted impurities. The process involves separating the feedstock by fractional distillation into a lower boiling fraction which contains the more volatile sulfur-containing aromatic impurities and at least one higher boiling fraction which contains the less volatile sulfur-containing aromatic impurities. Each fraction is then separately subjected to reaction conditions which are effective to convert at least a portion of its content of sulfur-containing aromatic impurities to higher boiling sulfur-containing products by alkylation with an alkylating agent in the presence of an acidic catalyst. The higher boiling sulfur-containing products are removed by fractional distillation. It is also stated that alkylation can be achieved in stages with the proviso that the conditions of alkylation are less severe in the initial alkylation stage than in a secondary stage, e.g., through the use of a lower temperature in the first stage as opposed to a higher temperature in a secondary stage.

[0014] U.S. Pat. No. 6,059,962 in the name of Bruce D. Alexander, George A. Huff, Vivek R. Pradhan, William J.

Reagan and Roger H. Clayton disclosed a product of reduced sulfur content wherein the product is produced in a multiple stage process from a feedstock which is comprised of a mixture of hydrocarbons and includes sulfur-containing aromatic compounds as unwanted impurities. The first stage involves: (1) subjecting the feedstock to alkylation conditions which are effective to convert a portion of the impurities to higher boiling sulfur-containing products, and (2) separating the resulting products by fractional distillation into a lower boiling fraction and a higher boiling fraction. The lower boiling fraction is comprised of hydrocarbons and is of reduced sulfur content relative to the feedstock. The higher boiling fraction is comprised of hydrocarbons and contains unconverted sulfur-containing aromatic impurities and also the higher boiling sulfur-containing products. Each subsequent stage involves: (1) subjecting the higher boiling fraction from the preceding stage to alkylation conditions which are effective to convert at least a portion of its content of sulfur-containing aromatic compounds to higher boiling sulfur-containing products, and (2) separating the resulting products by fractional distillation into a lower boiling hydrocarbon fraction and a higher boiling fraction which contains higher boiling sulfur-containing alkylation products. The total hydrocarbon product of reduced sulfur content from the process is comprised of the lower boiling fractions from various stages.

[0015] Another approach to reducing the sulfur-containing organic impurities content of a feedstock comprised of a normally liquid mixture of hydrocarbons which includes olefins is disclosed in International Publication Number WO 01/53432, A1. This approach involves (a) contacting the feedstock with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock; (b) fractionating the product from the olefin-modification reaction zone to produce: (i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is in the range from about 135° C. to about 221° C.; and (ii) a second fraction which is higher boiling than the first fraction and comprises sulfur-containing organic impurities; and (c) contacting the first fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in the sulfur-containing impurities of the first fraction to hydrogen sulfide.

[0016] It has now been discovered that the sulfur-containing organic impurities while undergoing reaction in the olefin-modification zone form refractive sulfur compounds. The formation of these refractive compounds is undesirable because they can only be treated by conventional hydrodesulfurization means which results in undesirable concomitant octane loss. These refractive sulfur compounds cannot be removed via a selective hydrotreating process. It has further been discovered that these refractive sulfur compounds concentrate in the fraction of the olefin-modification reaction zone product having a boiling range above about 200° C. The removal of these compounds can only be achieved through conventional hydrodesulfurization that results in the saturation of olefins and the loss of octane. Trace amounts of olefin-modification catalyst are also leached off of the catalyst in the olefin modification reaction zone and pass into the olefin-modification zone product. There is a potential for these compounds or components containing the leached

olefin-modification catalyst to cause both catalyst deactivation and pressure drop in any downstream units such as downstream hydrotreaters. Additionally it has been discovered that these compounds like the refractive sulfur compounds tend to concentrate in the 200° C. plus boiling range fraction.

[0017] By utilizing the process of the present invention the problems associated with refractive sulfur compounds and compounds or components containing leached olefin-modification catalyst can be ameliorated by fractionating the product from the olefin-modification zone into at least three fractions. The advantage of splitting the olefin-modification zone product into at least three fractions is that the refractive compounds and leached catalyst containing compounds or components can be recovered in a relatively small volume stream of the highest boiling fraction of the olefin modification zone product. The remainder of the olefin-modification zone product is split into at least two fractions wherein the lowest boiling fraction is relatively desulfurized and can be passed directly to the gasoline pool, and the intermediate boiling fraction can be passed to a selective hydrotreating zone, wherein the octane number is retained while the sulfur-containing organic impurities are converted to hydrogen sulfide. Although not preferred alternatively, the intermediate fraction can be passed to a conventional hydrotreater and subsequently to a reformer to upgrade the octane of this fraction. In accordance with the process of the invention the bulk of the olefin-modification zone effluent, e.g. 90 vol. % to 98 vol. %, can be split into two fractions containing a paucity of refractive sulfur and leached olefin modification catalyst and not be subjected to an octane reducing hydrodesulfurization step.

[0018] The highest boiling fraction, ideally, can be routed to a conventional diesel or naphtha hydrotreater or back to the fluidized catalytic cracking unit for removal of both the refractive and non-refractive sulfur compounds. The leached olefin-modification compounds or components can be removed with activated aluminum via conventional means known to those skilled in the art prior to being passed to the hydrotreater.

SUMMARY OF THE INVENTION

[0019] Hydrocarbon liquids which boil at standard pressure over either a broad or a narrow range of temperatures within the range from about 10° C. to about 345° C. are referred to herein as "hydrocarbon liquids." Such liquids are frequently encountered in the refining of petroleum and also in the refining of products from coal liquefaction and the processing of oil shale or tar sands, and these liquids are typically comprised of a complex mixture of hydrocarbons, and these mixtures can include paraffins, cycloparaffins, olefins and aromatics. For example, light naphtha, heavy naphtha, gasoline, kerosene and light cycle oil are all hydrocarbon liquids.

[0020] Hydrocarbon liquids which are encountered in a refinery frequently contain undesirable sulfur-containing impurities which must be at least partially removed. Hydrotreating procedures are effective and are commonly used for removing sulfur-containing impurities from hydrocarbon liquids. Unfortunately, conventional hydrotreating processes are usually unsatisfactory for use with highly olefinic hydrocarbon liquids because such processes result in

significant conversion of the olefins to paraffins which are usually of lower octane. In addition, the hydrogenation of the olefins results in the consumption of expensive hydrogen.

[0021] In accordance with International Publication Number WO 01/53432, A1 organic sulfur compounds can be removed from hydrocarbon liquids by a multiple step process which comprises (a) contacting the feedstock with an olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock;(b) fractionating the product into two fractions: namely a first fraction having a distillation endpoint of 135 C. to 221 C. and a higher boiling fraction; and (c) carrying out a hydrodesulfurization reaction with the lower boiling fraction.

[0022] Unfortunately such a process results in undesirable octane loss because the first fraction is subjected to conventional hydrotreating which serves to reduce octane via olefin saturation. Additionally such a process does not address or present a solution to the problems associated with converting refractive sulfur compounds to hydrogen sulfide while retaining octane. Further, such a process does not address the difficulties presented downstream of the olefin-modification zone by the leached catalyst compounds or components such as increased pressure drop and catalyst deactivation in downstream units.

[0023] Accordingly, there is a need for a process which can achieve a substantially complete removal of sulfur-containing impurities from olefin-containing hydrocarbon liquids which: (1) is relatively inexpensive to carry out, (2) results in little if any octane loss; and (3) addresses the problems associated with refractive sulfur compounds and leached catalyst compounds or components. For example, there is a need for such a process which can be used to remove sulfur-containing impurities from hydrocarbon liquids, such as products from a fluidized catalytic cracking process, which are highly olefinic and contain relatively large amounts of sulfur-containing organic materials such as mercaptans, thiophenic compounds, and benzothiophenic compounds as unwanted impurities.

[0024] It has now been discovered that such an improved process involves modifying the olefin content of the feedstock over an olefin-modification catalyst in an olefin-modification step, fractionating the products from the olefin-modification step into at least three fractions on the basis of boiling point, selectively hydrotreating the intermediate boiling fraction, and hydrodesulfurizing the highest boiling of the resulting fractions. The olefin-modification step results in a reduction of the olefinic unsaturation of the feedstock, as measured by bromine number. As a consequence of the olefin-modification step, a sulfur-lean product is obtained from the subsequent selective hydrotreating step which has little loss of octane relative to that of the feedstock to the olefin-modification step. In addition, the reduction of olefinic unsaturation in the olefin-modification step results in a corresponding reduction of hydrogen consumption in the respective selective hydrotreating and hydrodesulfurization steps since there is a reduced number of olefinic double bonds to consume hydrogen in hydrogenation reactions.

[0025] One embodiment of the invention is a process for producing a product of reduced sulfur content from a feedstock, wherein said feedstock contains sulfur-containing

organic impurities and is comprised of a normally liquid mixture of hydrocarbons which includes olefins, said process comprising:

[0026] (a) contacting the feedstock with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock;

[0027] (b) fractionating the product from said olefin-modification reaction zone to produce:

[0028] (i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 140° C.;

[0029] (ii) a second fraction which is higher boiling than the first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 240° C.; and

[0030] (iii) a third fraction which is higher boiling than the second fraction and comprises sulfur-containing organic impurities and refractive sulfur compounds;

[0031] (c) contacting the second fraction with a selective hydrotreating catalyst in the presence of hydrogen in a selective hydrotreating reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the second fraction to hydrogen sulfide; and

[0032] (d) contacting the third fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the third fraction to hydrogen sulfide.

[0033] Another embodiment of the invention is a process for producing products of reduced sulfur content from a feedstock, wherein said feedstock contains sulfur-containing organic impurities and is comprised of a normally liquid mixture of hydrocarbons which includes olefins, said process comprising:

[0034] (a) contacting the feedstock with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product which has a lower bromine number than that of the feedstock, wherein said olefin-modification catalyst is an acid catalyst;

[0035] (b) fractionating the product from said olefin-modification reaction zone to produce:

[0036] (i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 120° C.;

[0037] (ii) a second fraction which is higher boiling than the first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 200° C.; and;

[0038] (iii) a third fraction which is higher boiling than the second fraction and comprises sulfur-containing organic impurities and refractive sulfur compounds;

[0039] (c) contacting the second fraction with a selective hydrotreating catalyst in the presence of hydrogen in a selective hydrotreating reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the second fraction to hydrogen sulfide; and

[0040] (d) contacting the third fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the third fraction to hydrogen sulfide.

[0041] In another embodiment although not preferred, the second fraction can be passed to a hydrodesulfurization zone followed by a reforming zone to increase the octane number of the fraction which was reduced in the hydrodesulfurization zone.

[0042] An object of the invention is to provide an improved process for the removal of sulfur-containing impurities from a hydrocarbon liquid which contains a significant olefin content.

[0043] Another object of the invention is to provide an improved method for the efficient removal of sulfur-containing impurities from an olefinic cracked naphtha.

[0044] A further object of the invention is to provide an improved method for desulfurizing an olefinic cracked naphtha which yields a product of substantially unchanged octane.

[0045] Yet another object of the invention is to provide an improved method for handling problems associated with refractive sulfur compounds and leached catalyst compounds or components in a process for removing sulfur-containing impurities in a hydrocarbon liquid.

BRIEF DESCRIPTION OF THE DRAWING

[0046] The drawing is a schematic representation of an embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0047] A process for the production of a product of reduced sulfur content from an olefin-containing distillate hydrocarbon liquid which contains sulfur-containing impurities has been discovered. The process can be used to produce a product which is substantially free of sulfur-containing impurities, has a reduced olefin content, and has an octane which is similar to that of the feedstock.

[0048] The invention involves contacting the feedstock with an olefin-modification catalyst in a reaction zone under conditions which are effective to produce an intermediate product which has a reduced amount of olefinic unsaturation relative to that of the feedstock as measured by bromine number. The intermediate product is then separated into at least three fractions of different volatility. The fraction of highest volatility (i.e., the lowest boiling fraction) is relatively free of sulfur-containing organic impurities i.e. generally below 20 parts per million by weight sulfur and therefore can be passed directly to the gasoline pool. The second fraction or intermediate boiling range fraction, is contacted with a selective hydrotreating catalyst in the

presence of hydrogen under conditions effective to convert at least a portion of its sulfur-containing organic impurities to hydrogen sulfide. The hydrogen sulfide can be easily removed by conventional methods to provide a product of substantially reduced sulfur content relative to the feedstocks. The third fraction or highest boiling fraction is contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur-containing organic impurities and refractive sulfur compounds to hydrogen sulfide. The hydrogen sulfide can be easily removed by conventional methods to provide a product of substantially reduced sulfur content relative to the feedstocks.

[0049] Aromatic sulfur-containing impurities in the feedstock, such as thiophenic and benzothiophenic compounds, undergo conversion, at least in part, within the olefin-modification reaction zone to higher boiling sulfur-containing products some of which can be characterized as refractive sulfur compounds as further defined hereinafter. This conversion is believed to be a result of alkylation of the aromatic sulfur-containing impurities by olefins which is catalyzed by the olefin-modification catalyst. Upon fractionation of the effluent from the olefin-modification reaction zone, most of these high boiling sulfur-containing materials including the refractive sulfur compounds appear in the third boiling fraction or highest boiling fraction, and the first or lowest boiling fraction and the intermediate boiling fraction have a reduced sulfur content relative to that of the feedstock to the olefin-modification zone.

[0050] In a highly preferred embodiment, the second fraction is contacted with a selective hydrotreating catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of the fraction's sulfur-containing impurities to hydrogen sulfide. This can be accomplished by utilizing one of the selective hydrotreating processes that are presently being licensed such as the SCANfining process licensed by ExxonMobil Research and Engineering Company and the PRIME-G+ process licensed by IFP North America Inc. or by operating a conventional hydrotreating process at selective hydrotreating conditions that are relatively less severe such that the desulfurization occurs while limiting olefin saturation. Such selective hydrotreating processes are also disclosed in U.S. Pat. No. 6,007,704 (Chapus et al.), U.S. Pat. No. 5,821,397 (Joly et al.), and U.S. Pat. No. 6,255,548 (Didillon et al.)

[0051] The third fraction is contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of its sulfur-containing impurities including refractive sulfur compounds to hydrogen sulfide. A large portion of the sulfur-containing impurities of the higher boiling fraction or fractions will frequently be comprised of aromatic sulfur-containing compounds, such as thiophenic and benzothiophenic compounds and refractive sulfur compounds, which are more difficult to remove by hydrodesulfurization than mercaptans and thiophenic compounds. Accordingly, a preferred embodiment of the invention will comprise the use of more vigorous hydrodesulfurization conditions.

[0052] Feedstocks which can be used in the practice of this invention are comprised of normally liquid hydrocarbon mixtures which contain olefins and boil over a range of temperatures within the range from about 10° C. to about

345° C. as measured by the ASTM D 2887-97a procedure (which can be found in the 1999 Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels, Vol. 05.02, page 200, and said procedure is hereby incorporated herein by reference in its entirety) or by conventional alternative procedures. In addition, suitable feedstocks will preferably include a mixture of hydrocarbons which boils in the gasoline range. If desired, such feedstocks can also contain significant amounts of lower volatility hydrocarbon components which have a higher boiling point than said high volatility fraction. The feedstock will be comprised of a normally liquid mixture of hydrocarbons which desirably has a distillation endpoint which is about 345° C. or lower, and is preferably about 249° C. or lower. Preferably, the feedstock will have an initial boiling point which is below about 79° C. and a distillation endpoint which is not greater than about 345° C. Suitable feedstocks include any of the various complex mixtures of hydrocarbons which are conventionally encountered in the refining of petroleum, such as natural gas liquids, naphthas, light gas oils, heavy gas oils, and wide-cut gas oils, as well as hydrocarbon fractions which are derived from coal liquefaction and the processing of oil shale or tar sands. Preferred feedstocks are comprised of olefin-containing hydrocarbon mixtures which are derived from the catalytic cracking or the coking of hydrocarbon feedstocks.

[0053] Catalytic cracking products are highly preferred as a source of feedstock hydrocarbons for use in the subject invention. Materials of this type include liquids which boil below about 345° C., such as light naphtha, heavy naphtha and light cycle oil. However, it will also be appreciated that the entire output of volatile products from a catalytic cracking process can be utilized as a source of feedstock hydrocarbons for use in the practice of this invention. Catalytic cracking products are a desirable source of feedstock hydrocarbons because they typically have a relatively high olefin content and they usually contain substantial amounts of organic sulfur compounds as impurities. For example, a light naphtha from the fluidized catalytic cracking of a petroleum derived gas oil can contain up to about 60 wt. % of olefins and up to about 0.7 wt. % of sulfur wherein most of the sulfur will be in the form of thiophenic and benzothiophenic compounds. In addition, the sulfur-containing impurities will usually include mercaptans and organic sulfides. A preferred feedstock for use in the practice of this invention will be comprised of catalytic cracking products and will contain at least 1 wt. % of olefins. A preferred feedstock will be comprised of hydrocarbons from a catalytic cracking process and will contain at least 10 wt. % of olefins. A highly preferred feedstock will be comprised of hydrocarbons from a catalytic cracking process and will contain at least about 15 wt. % or 20 wt. % of olefins.

[0054] In one embodiment of the invention, the feedstock for the invention will be comprised of a mixture of low molecular weight olefins with hydrocarbons from a catalytic cracking process. For example, a feedstock can be prepared by adding olefins which contain from 3 to 5 carbon atoms to a naphtha from a catalytic cracking process.

[0055] In another embodiment of the invention, the feedstock for the invention will be comprised of a mixture of a naphtha from a catalytic cracking process with a source of volatile aromatic compounds, such as benzene and toluene. For example, a feedstock can be prepared by mixing a light

reformate with a naphtha from a catalytic cracking process. A typical light reformate will contain from about 0 to about 2 vol. % olefins, from about 20 to about 45 vol. % aromatics, and will have distillation properties such that the 10% distillation point ("T10") is no greater than about 160° F. (71° C.), the 50% distillation point ("T50") is no greater than about 200° F. (93° C.), and the 90% distillation point ("T90") is no greater than about 250° F. (121° C.). It will be understood that these distillation points refer to a distillation point obtained by the ASTM D 86-97 procedure (which can be found in the 1999 Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels, Vol. 05.01, page 16, and said procedure is hereby incorporated herein by reference in its entirety) or by conventional alternative procedures. A typical light reformate will contain from about 5 to about 15 vol. % of benzene.

[0056] Another embodiment of the invention involves the use of a feedstock which is comprised of a mixture of: (1) hydrocarbons from a catalytic cracking process; (2) a source of volatile aromatic compounds; and (3) a source of olefins which contain from 3 to 5 carbon atoms.

[0057] Suitable feedstocks for the invention will contain at least 1 wt. % of olefins, preferably at least 10 wt. % of olefins, and more preferably at least about 15 wt. % or 20 wt. % of olefins. If desired, the feedstock can have an olefin content of 50 wt. % or more. In addition, suitable feedstocks can contain from about 0.005 wt. % up to about 2.0 wt. % of sulfur in the form of organic sulfur compounds. However, typical feedstocks will generally contain from about 0.05 wt. % up to about 0.7 wt. % sulfur in the form of organic sulfur compounds.

[0058] Feedstocks which are useful in the practice of this invention, such as naphtha from a catalytic cracking process, will occasionally contain nitrogen-containing organic compounds as impurities in addition to the sulfur-containing impurities. Many of the typical nitrogen-containing impurities are organic bases and, in some instances, can cause a relatively rapid deactivation of the olefin-modification catalyst of the subject invention. In the event that such deactivation is observed, it can be prevented by removal of the basic nitrogen-containing impurities before they can contact the olefin-modification catalyst. Accordingly, when the feedstock contains basic nitrogen-containing impurities, a preferred embodiment of the invention comprises removing these basic nitrogen-containing impurities from the feedstock before it is contacted with the olefin-modification catalyst. In another embodiment of the invention, a feedstock is used which is substantially free of basic nitrogen-containing impurities (for example, such a feedstock will contain less than about 50 ppm by weight of basic nitrogen). A highly desirable feedstock is comprised of a treated naphtha which is prepared by removing basic nitrogen-containing impurities from a naphtha produced by a catalytic cracking process.

[0059] Basic nitrogen-containing impurities can be removed from the feedstock or from a material that is to be used as a feedstock component by any conventional method. Such methods typically involve treatment with an acidic material, and conventional methods include procedures such as washing with an aqueous solution of an acid or passing the material through a guard bed. In addition, a combination of such procedures can be used. Guard beds can be com-

prised of materials which include but are not limited to A-zeolite, Y-zeolite, L-zeolite, mordenite, fluorided alumina, fresh cracking catalyst, equilibrium cracking catalyst and acidic polymeric resins. If a guard bed technique is employed, it is often desirable to use two guard beds in such a manner that one guard bed can be regenerated while the other is in service. If a cracking catalyst is utilized to remove basic nitrogen-containing impurities, such a material can be regenerated in the regenerator of a catalytic cracking unit when it has become deactivated with respect to its ability to remove such impurities. If an acid wash is used to remove basic nitrogen-containing compounds, the treatment will be carried out with an aqueous solution of a suitable acid. Suitable acids for such use include but are not limited to hydrochloric acid, sulfuric acid and acetic acid. The concentration of acid in the aqueous solution is not critical, but is conveniently chosen to be in the range from about 0.1 wt. % to about 30 wt. %. For example, a 5 wt. % solution of sulfuric acid in water can be used to remove basic nitrogen containing impurities from a heavy naphtha produced by a catalytic cracking process.

[0060] The process of this invention is highly effective in removing sulfur-containing organic impurities of all types from the feedstock. Such impurities will typically include aromatic, sulfur-containing, organic compounds which include all aromatic organic compounds which contain at least one sulfur atom. Such materials include thiophenic and benzothiophenic compounds, and examples of such materials include but are not limited to thiophene, 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2,5-dimethylthiophene, 2-ethylthiophene, 3-ethylthiophene, benzothiophene, 2-methylbenzothiophene, 2,3-dimethylbenzothiophene, and 3-ethylbenzothiophene. Other typical sulfur-containing impurities include mercaptans and organic sulfides and disulfides.

[0061] The olefin-modification catalyst of the invention can be comprised of any material which is capable of catalyzing the oligomerization of olefins. Desirably, the olefin-modification catalyst will be comprised of a material which is also capable of catalyzing the alkylation of aromatic organic compounds by olefins. Conventional alkylation catalysts are highly suitable for use as the olefin-modification catalyst of this invention because they typically have the ability to catalyze both olefin oligomerization and the alkylation of aromatic organic compounds by olefins. Although liquid acids, such as sulfuric acid can be used, solid acidic catalysts are particularly desirable, and such solid acidic catalysts include liquid acids which are supported on a solid substrate. The solid catalysts are generally preferred over liquid catalysts because of the ease with which the feed can be contacted with such a material. For example, the feed can simply be passed through one or more fixed beds of solid particulate catalyst at a suitable temperature. Alternatively, the feed can be passed through an ebulated bed of solid particulate catalyst.

[0062] Olefin-modification catalysts which are suitable for use in the practice of the invention can be comprised of materials such as acidic polymeric resins, supported acids, and acidic inorganic oxides. Suitable acidic polymeric resins include the polymeric sulfonic acid resins which are well-known in the art and are commercially available. Amberlyst® 35, a product produced by Rohm and Haas Co., is a typical example of such a material.

[0063] Supported acids which are useful as olefin-modification catalysts include but are not limited to Brönsted acids (examples include phosphoric acid, sulfuric acid, boric acid, HF, fluorosulfonic acid, trifluoromethanesulfonic acid, and dihydroxyfluoroboric acid) and Lewis acids (examples include BF_3, BCl_3, $AlCl_3$, $AlBr_3$, $FeCl_2$, $FeCl_3$, $ZnCl_2$, SbF_5, $SbCl_5$ and combinations of $AlCl_3$ and HCl) which are supported on solids such as silica, alumina, silica-aluminas, zirconium oxide or clays. When supported liquid acids are employed, the supported catalysts are typically prepared by combining the desired liquid acid with the desired support and drying. Supported catalysts which are prepared by combining a phosphoric acid with a support are highly preferred and are referred to herein as solid phosphoric acid catalysts. These catalysts are preferred because they are both highly effective and low in cost. U.S. Pat. No. 2,921,081 (Zimmerschied et al.), which is incorporated herein by reference in its entirety, discloses the preparation of solid phosphoric acid catalysts by combining a zirconium compound selected from the group consisting of zirconium oxide and the halides of zirconium with an acid selected from the group consisting of orthophosphoric acid, pyrophosphoric acid and triphosphoric acid. U.S. Pat. No. 2,120,702 (Ipatieff et al.), which is incorporated herein by reference in its entirety, discloses the preparation of solid phosphoric acid catalysts by combining a phosphoric acid with a siliceous material. Finally, British Patent No. 863,539, which is incorporated herein by reference in its entirety, also discloses the preparation of a solid phosphoric acid catalyst by depositing a phosphoric acid on a solid siliceous material such as diatomaceous earth or kieselguhr.

[0064] With respect to a solid phosphoric acid that is prepared by depositing a phosphoric acid on kieselguhr, it is believed that the catalyst contains: (1) one or more free phosphoric acids (such as orthophosphoric acid, pyrophosphoric acid and triphosphoric acid) supported on kieselguhr; and (2) silicon phosphates which are derived from the chemical reaction of the acid or acids with the kieselguhr. While the anhydrous silicon phosphates are believed to be inactive as an olefin-modification catalyst, it is also believed that they can be hydrolyzed to yield a mixture of orthophosphoric and polyphosphoric acids which is active as an olefin-modification catalyst. The precise composition of this mixture will depend upon the amount of water to which the catalyst is exposed. In order to maintain a solid phosphoric acid alkylation catalyst at a satisfactory level of activity when it is used as an olefin-modification catalyst with a substantially anhydrous feedstock, it is conventional practice to add a small amount of an alcohol, such as isopropyl alcohol, to the feedstock to maintain the catalyst at a satisfactory level of hydration. It is believed that the alcohol undergoes dehydration upon contact with the catalyst, and that the resulting water then acts to hydrate the catalyst. If the catalyst contains too little water, it tends to have a very high acidity which can lead to rapid deactivation as a consequence of coking and, in addition, the catalyst will not possess a good physical integrity. Further hydration of the catalyst serves to reduce its acidity and reduces its tendency toward rapid deactivation through coke formation. However, excessive hydration of such a catalyst can cause the catalyst to soften, physically agglomerate, and create high pressure drops in fixed bed reactors. Accordingly, there is an optimum level of hydration for a solid phosphoric acid catalyst, and this level of hydration will be a function of the reaction

conditions. Although the invention is not to be so limited, with solid phosphoric acid catalysts, we have found that a water concentration in the feedstock which is in the range from abut 50 to about 1,000 ppm by weight will generally maintain a satisfactory level of catalyst hydration. If desired, this water can be provided in the form of an alcohol such as isopropyl alcohol which is believed to undergo dehydration upon contact with the catalyst.

[0065] Acidic inorganic oxides which are useful as olefin-modification catalysts include but are not limited to aluminas, silica-aluminas, natural and synthetic pillared clays, and natural and synthetic zeolites such as faujasites, mordenites, L, omega, X, Y, beta, and ZSM zeolites. Highly suitable zeolites include beta, Y, ZSM-3, ZSM-4, ZSM-5, ZSM-18, and ZSM-20. If desired, the zeolites can be incorporated into an inorganic oxide matrix material such as a silica-alumina.

[0066] Olefin-modification catalysts can comprise mixtures of different materials, such as a Lewis acid (examples include BF_3, BCl_3, SbF_5 and $AlCl_3$), a nonzeolitic solid inorganic oxide (such as silica, alumina and silica-alumina), and a large-pore crystalline molecular sieve (examples include zeolites, pillared clays and aluminophosphates).

[0067] In the event that a solid olefin-modification catalyst is used, it will desirably be in a physical form which will permit a rapid and effective contacting with feed in the olefin-modification reaction zone. Although the invention is not to be so limited, it is preferred that a solid catalyst be in particulate form wherein the largest dimension of the particles has an average value which is in the range from about 0.1 mm to about 2 cm. For example, substantially spherical beads of catalyst can be used which have an average diameter from about 0.1 mm to about 2 cm. Alternatively, the catalyst can be used in the form of rods which have a diameter in the range from about 0.1 mm to about 1 cm and a length in the range from about 0.2 mm to about 2 cm.

[0068] In the practice of the invention, the feedstock is contacted with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock without causing any significant cracking of any paraffins in the feedstock. It will be understood that the "bromine number" referred to herein is preferably determined by the ASTM D 1159-98 procedure, which can be found in the 1999 Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels, Vol. 05.01, page 407, and said procedure is hereby incorporated herein by reference in its entirety. However, other conventional analytical procedures for the determination of bromine number can also be used. The bromine number of the product from the olefin-modification reaction zone will desirably be no greater than 80% that of the feedstock to said reaction zone, preferably no greater than 70% that of said feedstock, and more preferably no greater than 65% that of said feedstock.

[0069] The reaction zone can consist of one or more fixed bed reactors containing the same or different catalysts. A fixed reactor can also comprise a plurality of catalyst beds. The plurality of catalyst beds in a single fixed bed reactor can also comprise the same or different catalysts.

[0070] The conditions utilized in the olefin-modification reaction zone are also preferably selected so that at least a

portion of the olefins in the feedstock is converted to products which are of a suitable volatility to be useful as components of fuels, such as gasoline and diesel fuels.

[0071] Although the invention is not to be so limited, it is believed that the olefins in the feedstock to the olefin-modification reaction zone are at least partially consumed in a variety of chemical reactions upon contact of the feedstock with the olefin-modification catalyst in said zone. And it is believed that the specific chemical reactions will depend upon the composition of the feedstock. These chemical processes are believed to include olefin polymerization and the alkylation of aromatic compounds by olefins.

[0072] The condensation reaction of an olefin or a mixture of olefins over an olefin-modification catalyst to form higher molecular weight products is referred to herein as a polymerization process, and the products can be either low molecular weight oligomers or high molecular weight polymers. Oligomers are formed by the condensation of 2, 3 or 4 olefin molecules with each other, while polymers are formed by the condensation of 5 or more olefin molecules with each other. As used herein, the term "polymerization" is used to broadly refer to a process for the formation of oligomers and/or polymers. Olefin polymerization results in a consumption of olefinic unsaturation. For example, the simple condensation of two molecules of propene results in the formation of a six carbon olefin which has only a single olefinic double bond (2 double bonds in the starting materials have been replaced by 1 double bond in the product). Similarly, the simple condensation of three molecules of propene results in the formation of a nine carbon olefin which has only a single olefinic double bond (3 double bonds in the starting materials have been replaced by 1 double bond in the product).

[0073] Although olefin polymerization is a simple model for understanding the reduction in bromine number that occurs in the olefin-modification reaction zone, it is believed that other processes are also important. For example, the initial products of simple olefin condensation can undergo isomerization in the presence of the olefin-modification catalyst to yield highly branched monounsaturated olefins. In addition, polymerization reactions may occur to yield polymers which subsequently undergo fragmentation in the presence of the olefin-modification catalyst to yield highly branched products which are of a lower molecular weight than the initial polymerization product. Although the invention is not to be so limited, it is believed that the following transformations occur within the olefin-modification reaction zone: (1) olefins in the feedstock which are of low molecular weight are converted to olefins of higher molecular weight which are both highly branched and within the gasoline boiling range; and (2) unbranched or modestly branched olefins in the feedstock are isomerized to highly branched olefins which are within the gasoline boiling range.

[0074] The alkylation of aromatic compounds is also an important chemical process which can occur in the olefin-modification reaction zone and acts to reduce the bromine number of the feedstock. The alkylation of an aromatic organic compound by an olefin, which contains a single double bond, results in the destruction of the double bond of the olefin and results in the substitution of an alkyl group for a hydrogen atom on the aromatic ring system of the sub-

strate. This destruction of the olefinic double bond of the olefin contributes to the formation of a product in the olefin-modification reaction zone which has a reduced bromine number relative to that of the feedstock. However, aromatic organic compounds vary widely in their reactivity as alkylation substrates. For example, the relative reactivities of some representative aromatic compounds toward alkylation by 1-heptene at 204° C. over a solid phosphoric acid catalyst are set forth in Table I, wherein each rate constant was derived from the slope of the line obtained by plotting experimental data in the form of ln(1−x) as a function of time where x is the substrate concentration.

[0075] As used herein, the term "sulfur-containing aromatic compound" and "sulfur-containing aromatic impurity" refer to any aromatic organic compound which contains at least one sulfur atom in its aromatic ring system. Such materials include thiophenic and benzothiophenic compounds.

[0076] Sulfur-containing aromatic compounds are usually alkylated more rapidly than aromatic hydrocarbons. Accordingly, the sulfur-containing aromatic impurities can, to a limited degree, be selectively alkylated in the olefin-modification reaction zone. However, if desired, the reaction conditions in the reaction zone can be selected so that significant alkylation of aromatic hydrocarbons does take place. This embodiment of the invention can be very useful if the feedstock contains volatile aromatic hydrocarbons, such as benzene, and it is desired to destroy such material by conversion to higher molecular weight alkylation products. This embodiment is particularly useful when the feedstock contains significant amounts of low molecular weight olefins, such as olefins which contain from 3 to 5 carbon atoms. The products from mono- or dialkylation of benzene with such low molecular weight olefins will contain from 9 to 16 carbon atoms and, accordingly, will be of sufficient volatility to be useful as components of gasoline or diesel fuels.

TABLE I

Alkylation Rate Constants for Various Aromatic
Substrates upon Reaction with 1-Heptene at 204° C.
over a Solid Phosphoric Acid Catalyst.

Compound	Rate Constant, min⁻¹
Thiophene	0.077
2-Methylthiophene	0.046
2,5-Dimethylthiophene	0.004
Benzothiophene	0.008
Benzene	0.001
Toluene	0.002

[0077] The alkylation of sulfur-containing aromatic impurities in the feedstock to the olefin-modification reaction zone results in the formation of higher boiling sulfur-containing products. Accordingly, such materials can be removed by fractionation of the reaction zone effluent on the basis of boiling point. As a very crude approximation, each carbon atom in the side chain of a monoalkylated thiophene adds about 25° C. to the 84° C. boiling point of thiophene. As an example, 2-octylthiophene has a boiling point of 250° C., which corresponds to a boiling point increase of 23° C. over that of thiophene for each carbon atom in the eight carbon alkyl group. Accordingly, monoalkylation of thiophene with a C₃ to C₅ olefin in the olefin-modification

reaction zone will usually yield a sulfur-containing alkylation product which has a high enough boiling point to be easily removed by fractional distillation as a component of a high boiling fraction which has an initial boiling point of about 210° C.

[0078] The alkylation of a sulfur-containing aromatic compound by an olefin is illustrated by the mono-alkylation of thiophene with propene to yield either 2-isopropylth-iophene or 3-isopropylthiophene. The higher molecular weight of such an alkylation product is reflected by a higher boiling point relative to that of the starting material. In one embodiment of the invention, reaction conditions in the olefin-modification reaction zone are selected so that a major portion of any sulfur-containing aromatic impurities in the feedstock are converted to higher boiling sulfur-containing products.

[0079] Mercaptans are a class of organic sulfur-containing compounds which frequently appear in significant quantity as impurities in the hydrocarbon liquids which are conventionally encountered in the refining of petroleum. For example, straight run gasolines, which are prepared by simple distillation of crude oil, will frequently contain significant amounts of mercaptans and sulfides as impurities. In addition, benzothiophenic compounds and some multi-substituted thiophenes, such as certain 2,5-dialkylth-iophenes, will also be relatively unreactive under the conditions employed in the olefin-modification reaction zone. Accordingly, a large proportion of the mercaptans in the feedstock and significant amounts of certain relatively unreactive sulfur-containing aromatic compounds can survive the reaction conditions in the olefin-modification reaction zone.

[0080] In the practice of this invention, the feedstock is contacted with the olefin-modification catalyst within the olefin-modification reaction zone at a temperature and for a period of time which are effective to result in the desired reduction of the feedstock's olefinic unsaturation as measured by bromine number. The contacting temperature will be desirably in excess of about 50° C., preferably in excess of 100° C. and more preferably in excess of 125° C. The contacting will generally be carried out at a temperature in the range from about 50° C. to about 350° C., preferably from about 100° C. to about 350° C., and more preferably from about 125° C. to about 250° C. It will be appreciated, of course, that the optimum temperature will be a function of the olefin-modification catalyst used, the olefin concentration in the feedstock, the type of olefins present in the feedstock, and the type of aromatic compounds in the feedstock that are to be alkylated.

[0081] The feedstock can be contacted with the olefin-modification catalyst in the olefin-modification reaction zone at any suitable pressure. However, pressures in the range from about 0.01 to about 200 atmospheres are desirable, and a pressure in the range from about 1 to about 100 atmospheres is preferred. When the feedstock is simply allowed to flow through a catalyst bed, it is generally preferred to use a pressure at which the feed will be a liquid.

[0082] In a highly preferred embodiment of the invention, the conditions utilized in the olefin-modification reaction zone are selected so that no significant cracking of paraffins in the feedstock takes place. For example, desirably less than 10% of the paraffins in the feedstock will be cracked,

preferably less than 5% of the paraffins will be cracked, and more preferably less than 1% of the paraffins will be cracked. It is believed that any significant cracking of paraffins will result in the formation of undesirable by-products, for example, the formation of low molecular weight compounds which results in gasoline volume loss.

[0083] In the practice of the invention, the effluent from the olefin-modification reaction zone is fractionated on the basis of volatility into at least three fractions.

[0084] The distillation initial boiling point of the highest boiling third fraction is desirably greater than about 200° C.

[0085] This fraction will contain a concentration of various compounds that can cause rapid catalyst deactivation in downstream selective and conventional hydrotreaters. Specifically, in the olefin-modification reaction zone, refractive sulfur species are created. These refractive sulfur compounds concentrate in the 200° C. plus fraction of the olefin-modification zone product. The removal of these compounds can only be accomplished via conventional hydrotreating or hydrodesulfurization which also detrimentally results in the saturation of olefins causing octane loss.

[0086] It is believed these refractive sulfur compounds have the following structure:
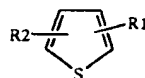
[0087] Where R2 and R1 must have two or more carbons, e.g. C2H5, C3H7 etc. and one chain must have more than five carbons, e.g. C5H11, C6H13, etc.

[0088] Thus examples of refractive sulfur compounds are:
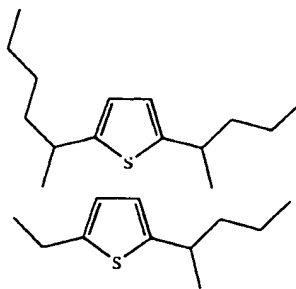
[0089] It is believed refractive sulfur is a thiophene containing seven or more alkyl carbons.

[0090] Additionally, trace amounts of the olefin-modification catalyst can be leached off in the olefin-modification zone and enter the olefin-modification zone product. This leached catalyst can cause catalyst deactivation and/or pressure drop difficulties in any downstream selective hydrotreater or hydrodesulfurization reactor. This leached catalyst tends to concentrate in the 200° C. plus boiling fraction.

[0091] Other undesirable compounds that concentrate in the 200° C. plus boiling range fraction include nitrogen-containing compounds and dienes.

[0092] The advantage of the process of the invention is that these compounds can be recovered in the relative small volume of the 200° C. plus fraction. The volume of this fraction can range from 2 volume percent to 10 volume percent of the olefin-modification zone product. Preferably, this volume percent can range from 2 volume percent to 6 volume percent.

[0093] Thus the bulk, e.g., 90-98 volume percent, of the olefin-modification product, can be split into two fractions. The 140° C. minus, or more preferably the 120 ° C. minus boiling range first or lowest boiling fraction can be routed directly to gasoline. The lowest boiling range first fraction is typically sulfur free such that it contains less than about 50 parts per million by weight sulfur and preferably less than 30 parts per million by weight sulfur and most preferably less than 20 parts per million by weight, and can therefore be directly used as blending stock for gasoline.

[0094] The intermediate fraction or second boiling fraction, preferably has a distillation end point of less than about 240° C. and most preferably less than about 200° C. The intermediate or second boiling fraction is passed to a selective hydrotreating zone that removes sulfur compounds while retaining the octane.

[0095] The highest boiling fraction, which has a boiling range higher than the intermediate fraction, from fractionation of the product from the olefin-modification reaction zone is contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur in its sulfur-containing organic impurities including the refractive sulfur compounds to hydrogen sulfide. In a highly preferred embodiment, at least a portion of the higher boiling fraction or fractions are also contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur in its sulfur-containing organic impurities to hydrogen sulfide. Alternatively the highest boiling fraction can be recycled to the fluidized catalytic cracking unit.

[0096] The hydrodesulfurization catalyst can be any conventional catalyst, for example, a catalyst comprised of a Group VI and/or a Group VIII metal which is supported on a suitable substrate. The Group VI metal is typically molybdenum or tungsten, and the Group VIII metal is typically nickel or cobalt. Typical combinations include nickel with molybdenum and cobalt with molybdenum. Suitable catalyst supports include, but are not limited to, alumina, silica, titania, calcium oxide, magnesia, strontium oxide, barium oxide, carbon, zirconia, diatomaceous earth, and lanthanide oxides. Preferred catalyst supports are porous and include alumina, silica, and silica-alumina.

[0097] The particle size and shape of the hydrodesulfurization catalyst will typically be determined by the manner in which the reactants are contacted with the catalyst. For example, the catalyst can be used as a fixed bed catalyst or as an ebulating bed catalyst.

[0098] The hydrodesulfurization reaction conditions used in the practice of this invention are conventional in character. For example, the pressures can range from about 15 to about 1500 psi (about 1.02 to about 102.1 atmospheres); the temperature can range from about 50° C. to about 450° C., and the liquid hourly space velocity can range from about

0.5 to about 15 LHSV. The ratio of hydrogen to hydrocarbon feed in the hydrodesulfurization reaction zone will typically range from about 200 to about 5000 standard cubic feet per barrel. The extent of hydrodesulfurization will be a function of the hydrodesulfurization catalyst and reaction conditions selected and also the precise nature of the sulfur-containing organic impurities in the feed to the hydrodesulfurization reaction zone. However, the hydrodesulfurization process conditions will be desirably selected so that at least about 50% of the sulfur content of the sulfur-containing organic impurities is converted to hydrogen sulfide, and preferably so that the conversion to hydrogen sulfide is at least about 75% or more.

[0099] After removal of hydrogen sulfide, the product from hydrodesulfurization of the highest boiling fraction from the olefin-modification reaction zone will have a sulfur content which is desirably less than 50 ppm by weight, preferably less than 30 ppm by weight, and more preferably less than 10 ppm by weight. The octane of this hydrodesulfurization product will be desirably at least 90% that of the feedstock to the olefin-modification reaction zone, preferably at least 95% that of said feedstock, and more preferably at least 97% that of said feedstock. Unless otherwise specified, the term octane as used herein refers to an (R+M)/2 octane, which is the sum of a material's research octane and motor octane divided by 2.

[0100] The intermediate boiling second fractionation product of the effluent from the olefin-modification reaction zone is contacted with a selective hydrotreating catalyst in the presence of hydrogen under conditions which are effective to selectively convert at least a portion of the sulfur in its sulfur-containing organic impurities to hydrogen sulfide with minimum hydrogenation of olefins.

[0101] One such selective hydrotreating process called SCANfining™ is licensed by ExxonMobil Research and Engineering Company. The SCANfining Process is a catalytic desulfurization process that utilizes a catalyst designated as RT 225 to selectively remove sulfur from fluidized catalytic cracking naphtha with minimum hydrogenation of olefins, hereby preserving octane. Yet another selective hydrotreating process is called PRIME-G+™ and is licensed by IFP North America, Inc. This process enables over 98% desulfurization of FCC naphtha while maximizing octane barrel by limiting olefin saturation. Another method for effecting the selective hydrotreating process in accordance with the process of the present invention is to contact the intermediate boiling second fraction with conventional hydrotreating catalyst at selective hydrotreating zone conditions which are generally less severe or milder than conventional hydrotreating conditions. The selective hydrotreating zone conditions include a temperature in the range of form about 100° C. to about 300° C., a pressure range form about 300 psig to about 600 psig, and a liquid hourly space velocity in the range of about 3 to about 10. The ratio of hydrogen to hydrocarbon feed in the selective hydrotreating zone will range from about 700 to about 2000 standard cubic feet per barrel of feed.

[0102] After the carrying out the selective hydrotreating step and removing hydrogen sulfide, the intermediate boiling fraction will have a sulfur content which is desirably less than about 50 ppm by weight, preferably less than 30 ppm by weight, and more preferably less than 10 by weight. The

octane of this intermediate fraction selective hydrotreating process will desirably be at least 95 percent of that of the feedstock to the olefin-modification zone, preferably at least 97 percent and most preferably 98 percent of that of the subject feedstock.

[0103] One embodiment of the invention is schematically illustrated in the drawing. With reference to the drawing, total catalytic naphtha from a fluidized catalytic cracking process is passed through line 1 into pretreatment vessel 2. The naphtha feedstock is comprised of mixture hydrocarbons which include olefins, paraffins, naphthenes, and aromatics, and the olefin content is in the range from about 10 wt. % to about 60 wt. %. In addition, the naphtha feedstock contains from about 0.2 wt. % to about 0.5 wt. % sulfur in the form of sulfur-containing organic impurities, which include thiophene, thiophene derivatives, benzothiophene and benzothiophene derivatives, mercaptans, sulfides and disulfides. The feedstock also contains from about 5 to about 200 ppm by weight of basic nitrogen containing impurities.

[0104] The basic nitrogen containing impurities are removed from the feedstock in pretreatment vessel 2 through contact with an acidic material, such as an aqueous solution of sulfuric acid, under mild contacting conditions which do not cause any significant chemical modification of the hydrocarbon components of the feedstock.

[0105] Effluent from pretreatment vessel 2 is passed through line 3 and is introduced into olefin-modification reactor 4, which contains an olefin-modification catalyst. The feed to reactor 4 passes through the reactor where it contacts the olefin-modification catalyst under reaction conditions which are effective to produce a product having a bromine number which is lower than that of the feed from line 3. In addition, a substantial portion of the thiophenic and benzothiophenic impurities are converted to higher boiling sulfur-containing material including refractive sulfur compounds through alkylation by the olefins in the feed.

[0106] The products from olefin-modification reactor 4 are discharged through line 5 and are passed to distillation column 6 where these products are fractionally distilled. A high boiling fraction, which comprises a hydrocarbon mixture which contains alkylated sulfur-containing impurities including refractive sulfur compounds and leached catalyst compounds or components, is withdrawn from distillation column 6 through line 7. An intermediate boiling fraction, which is of reduced sulfur content relative to the sulfur content of the original heavy naphtha feedstock and has a distillation endpoint less than about 240 C., is withdrawn from distillation column 6 through line 8. The lowest boiling fraction is withdrawn from distillation column 6 through line 9.

[0107] The highest boiling third fraction from distillation column 6 is passed through line 7 and is introduced into hydrodesulfurization reactor 11, and hydrogen is introduced into reactor 11 through line 10. This third fraction is contacted with a hydrodesulfurization catalyst within reactor 11 in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur in the sulfur-containing impurities of the feed from line 7 to hydrogen sulfide. A product is withdrawn from reactor 11 through line 12 which, after removal of hydrogen sulfide, has a reduced sulfur content relative to that of the feed from line 7. The sulfur content of this product will, typically, be less than about 30 ppm by weight.

[0108] The intermediate boiling fraction from distillation column 6 is passed through line 8 and is introduced into selective hydrotreating reactor 14, and hydrogen is introduced into reactor 14 through line 13. The intermediate fraction is contacted with a selective hydrotreating catalyst within reactor 14 in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur in the sulfur-containing impurities of the feed from line 8 to hydrogen sulfide. A product is withdrawn from reactor 14 through line 15 which, after removal of hydrogen sulfide, has a reduced sulfur content relative to both the heavy naphtha feedstock to the process and the feed from line 8. The sulfur content of this product will, typically, be less than about 30 ppm by weight.

[0109] The lowest boiling first fraction is withdrawn from the distillation column 6 through line 9. The sulfur content of this fraction will typically be 10 ppm by weight.

[0110] The following examples are intended only to illustrate the invention and is not to be construed as imposing limitations on the invention.

EXAMPLE 1

[0111] A naphtha feedstock having the following analysis was contacted in an olefin-modification zone in accordance with the present invention.

TABLE 11

S, ppm	580
Basic N, ppm	less than 5
Total N, ppm	10
Mercaptan S, ppm	53
RVP, psia	7.41
RON	92.4
MON	79.8
R + M/2	86.1
ASTM D86 Distillation	
IBP ° C.	102.7
FBP ° C.	269.9
Peak Group Information, ppm	
Thiophene	117.55
C1 Thiophene	253.58
C2 + Thiophenes	128.6

[0112] The olefin-modification zone consisted of two stages of fixed bed of solid phosphoric acid (obtained from Sud Chemie and sold under the name C84-5-01) and was operated at a temperature of 172° C. in the first stage and 122° C. in the second stage, a pressure of 500 psig and a liquid hourly space velocity of 1.5 LHSV.

[0113] The resulting olefin-modification reaction zone product was fractionally distilled into three fractions in accordance with the process of the invention and two fractions for comparative purposes.

[0114] Distillations of the olefin-modification zone products were carried out on a Fischer 800 Bench-scale semi-automatic distillation unit in accordance with the ASTM D2892 method.

[0115] The sample was heated in a three-liter flask with magnetic stirrer, under a Nitrogen bleed.

[0116] Fractionation took place in a column of 18 mm diameter packed with 4 mm Pro-pak gauze packing to give an efficiency of 15 theoretical plates.

[0117] The vapor was liquefied on a condenser chilled to −20 C, and the distillate taken-off at a ratio of 20:4 via a timed reflux divider into a chilled receiver.

[0118] The temperature cut point was determined by measuring the vapor temperature with a resistance thermometer and associated electronic meter.

[0119] The unit had the capacity to distil under vacuum, but in this case samples were distilled at atmospheric pressure, with temperatures corrected to 760 mm.

[0120] Distillation products were purged with nitrogen and stored under refrigeration prior to further testing.

[0121] The following Table III shows the relative amounts olefin-modification catalyst ("phosphorous"), total sulfur in comparative boiling range fractions: 100° C.−, and 100° C.+ and the three boiling range fractions in accordance with the present invention: 100° C.−, 100° C. to 200° C., and 200° C.+.

TABLE IV

S, ppm	450
Basic N, ppm	less than 5
Total N, ppm	13
Mercaptan S, ppm	4
RVP	11.12
RON	94.4
MON	80.1
R + M/2	87.3
ASTM D86 Distillation	
IBP ° C.	87.6
FBP ° C.	255.8
Peak Group Information, ppm	
Thiophene	156.43
C1 Thiophenes	179.91
C2 + Thiophenes	37.4

TABLE III

Two Cut Splitter vs. Three Cut Splitter Product Contaminants

	Total Sulfur (ppm)	Normal Sulfur (ppm)	Refractive Sulfur (ppm)	Phosphorous (ppm)	Nitrogen (ppm)	Bromine No.	Yields Wt %
Feed	580	580	0	<0.2	10	84.9	100
Two Cut Splitter							
OVHD: (IBP/100° C.)	10.6	10.6	0	<0.2	<0.3	62.3	49.9
Bottoms: (100° C.+)	1140	440	700	13.6	7.1	83.8	50.1
Three Cut Splitter							
OVHD (IBP/100° C.)	158	155	3	<0.2	<0.3	62.3	49.9
Sidedraw: (100° C./200° C.)	359	352	7	<0.2	0.5	64.8	39.1
Bottoms: (200° C.)	3970	651	3319	61.1	33	117	11

[0122] As can be observed form the above table the phosphorus and refractive sulfur is preferentially concentrated in the highest boiling range fraction when the olefin modification zone effluent is split into three fractions in accordance with the present invention. This highest boiling range is of relatively small volume, i.e., 11% wt. % yield and therefore permits a much smaller fraction of the olefin modification zone product to being treated by the octane reducing, hydrodesulfurization process. Note in the comparative bottoms fraction, the yield is 50.1 wt. % which means that one half of the olefin-modification stream effluent would have to be hydrotreated nonselectively to remove refractive sulfur resulting in undesirable octane loss for one-half of the stream verses 11% of the stream in accordance with the process of the invention.

EXAMPLE 2

[0123] A naphtha feedstock having the following analysis was contacted in an olefin-modification zone in accordance with the present invention.

[0124] The above feedstock was contacted in an olefin modification zone comprising fixed bed of solid phosphoric acid (obtained from Sud Chemie and sold under the name C84-5-01). The olefin-modification zone was operated at a temperature of 193° C., a pressure of 250 psig and a liquid hourly space velocity of 1.5.

[0125] The reaction zone product was fractionated into three fractions in accordance with the present invention and two fractions for comparative purposes in a unit having the following characteristics:

pot volume:	~1500 gallons
column height:	34'6"
column diameter:	12" with structured packing
number of theoretical plates:	33

[0126] With respect to the three fractions, the product was atmospherically distilled to a head temperature of 100° C. The take-off ratios were 33 percent until head temperature equaled 80° C., 14 percent until head temperature equaled 90° C., 8 percent until head temperature equaled 100° C. The

system was then set for total reflux return. The receiver containing the IBP-100° C. fraction was cut. The system was then pulled under vacuum to 55 mmHG and take-off initiated. The take-off ratios were between 5 percent and 8 percent during the 100-200° C. cut. The system was shutdown when the head temperature reached 106° C. at 55 mmHG. The 100-200° C. fraction, pot fraction 200-FBP and vacuum trap fraction were cut.

[0127] The comparative two fraction splitting was carried out in an analogous way resulting in a IBP to 100° C. fraction and a 100° C.+ fraction.

[0128] The following table shows the sulfur distribution in the respective three fractions prepared in accordance with the present invention. It should be noted that the fractionation that was carried out was less than ideal, because the IBP-100° C. fraction shows the presence of C3+ thiophenes which would ordinarily not be present in this fraction.

TABLE V

Sulfur Distribution Per Fraction			
Components	IBP-100° C.	100° C.–200° C.	200° C.+
H2S	0	0	0
Mercaptans + 1 Coeluting Unknown	17.81	0	0
Sulfides	3.17	6.33	0
Disulfides	0.72	0	0
Sulfoxides/Sulfones	0	0	0
Thiophene	11.16	0	0
Tetrahydrothiophene & Me-Thiophene	1.45	20.08	0
C1 Thiophene	6.59	31.38	0
C2 Thiophene	2.58	66.14	0
C3 + C4 Thiophenes	2.33	75.02	0.63
C5 Thiophene	3.72	179.93	12.39
C6 Thiophene	5.24	35.74	919.06
C7 Thiophene	3.77	2.18	412.21
C8 + C9 Thiophene	2	0.25	410.2
C10 Thiophene	2.19	0	549.25
C11 Thiophene	1.34	0	477.88
C12 Thiophene	0.74	0	743.41
Unknowns	1.62	3.44	0

[0129] The comparative 100° C.+ fraction was subjected to conventional hydrotreating at the following conditions:

[0130] 318° C.

[0131] 450 psig

[0132] 3 LHSV

[0133] The side-cut or 100° C. to 200° C. fraction obtained in accordance with the present invention was subjected to a hydrotreating step at selective hydrotreating conditions including:

[0134] 307° C.

[0135] 450 psig

[0136] 3 LHSV

[0137] The hydrotreating unit was a fixed bed, downflow hydrotreating pilot plant configured for once-through processing of naphtha or distillate feeds at hydrogen pressures up to 2000 psig, hydrogen flows to 5 scfh, liquid feed rates to 600 cc/hr and temperatures to 800 deg. F. The reactor was approximately 0.96" idx18" long and can hold up to a 120

cc of catalyst charge and is heated by a salt bath. The internal catalyst bed temperature was monitored by a programmable traversing single point thermocouple. An LDC ConstaMetric 3200 precision metering pump pumps the feed in and hydrogen flow into the unit through a Brooks mass flow meter. The combined liquid and gas flows were passed through the downflow reactor and are separated in a Strahman sight gage glass. The offgas pressure is controlled via a Rosemount pressure transmitter and Badger control valve where the offgas flow goes through a caustic scrubber and is measured downstream at atmospheric pressure via an Alexander Wright wet test meter. The liquid product in the separator had a level control via Rosemount differential transmitter and a Badger control valve. The product was cooled via a tube in tube heat exchanger and collected in a refrigerator through an automated valve manifold, sequenced by computer control into one of three product receivers. The computer control/data collection was done via Analog Devices uMac 6000 and automated safeguard shutdowns were controlled via a Siemens Simatic TI505 PLC.

[0138] Table VI below shows the octane retention afforded by the invention while effecting deep desulfurization. Note that the sulfur level in the combined overhead "OVHD" and intermediate fraction "Sidedraw" would have been significantly lower had the fractionation been carried out ideally. Specifically, the combined first and second fractions ("OVHD" and "Sidedraw") show an octane loss of 87.3 to 84.5 with a desulfurization of down to 50 ppm, wt, while the comparative process only desulfurizes to 60 ppmw for a similar octane loss. The results would have been more significant had the fractionation been more ideal. Further, in order to achieve the product sulfur in the comparative combined fraction, the hydrodesulfurization conditions would have to be substantially more severe and would be:

[0139] 332° C.

[0140] 450 psig

[0141] 1.5 LHSV

[0142] These more severe conditions would result in further octane loss on 33.1% of the stream.

TABLE VI

Two Cut Splitter vs. Three Cut Splitter Octane Retention			
	Sulfur (ppm)	Octane	Wt. % Yields
Feed	450	87.3	100
Two Cut Splitter			
OVHD: (IBP/100° C.)	69	86.1	66.9
Bottoms: (100° C.+)	70	82.4	33.1
Combined Product	69	84.9	100
Three Cut Splitter			
OVHD: (IBP/100° C.)	69	86.1	66.9
Sidedraw: (100° C./200° C.)	15	80	24.6
Bottoms: (200° C.)			8.5
OVHD/SD Combined Product	50	84.5	91.5

We claim:

1. A process for producing a product of reduced sulfur content from a feedstock, wherein said feedstock contains

sulfur-containing organic impurities and is comprised of a normally liquid mixture of hydrocarbons which includes olefins, said process comprising:

(a) contacting the feedstock with an olefin-modification catalyst in at least one olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock and wherein the product contains refractive sulfur compounds;

(b) fractionating the product from said olefin-modification reaction zone to produce:

(i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which less than about 140° C.;

(ii) a second fraction which is higher boiling than the first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 240° C.; and

(iii) a third fraction which is higher boiling than the second fraction and comprises sulfur-containing organic impurities and refractive sulfur compounds;

(c) contacting said second fraction with a selective hydrotreating catalyst in the presence of hydrogen in a selective hydrotreating reaction zone under conditions which are effective to convert at least a portion of the sulfur as containing impurities in the second fraction to hydrogen sulfide; and

(d) contacting said third fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the third fraction to hydrogen sulfide.

2. The process of claim 1 wherein the feedstock contains paraffins and wherein the conditions in said olefin-modification reaction zone are effective to produce a product having a bromine number which is lower than that of the feedstock and less than 10% of the paraffins in the feedstock are cracked.

3. The process of claim 1 which additionally comprises removing hydrogen sulfide from the effluent of said selective hydrotreating reaction zone to yield a desulfurized product which contains less than about 50 parts per million by weight of sulfur.

4. The process of claim 3 wherein the octane of the desulfurized product is at least 95% that of the feedstock to the olefin-modification reaction zone.

5. The process of claim 1 wherein the feedstock contains from about 0.05 wt. % to about 0.7 wt. % of sulfur in the form of organic sulfur compounds.

6. The process of claim 1 which additionally comprises removing hydrogen sulfide from the effluent of said hydrodesulfurization reaction zone to yield a desulfurized product which contains less than about 50 parts per million by weight sulfur.

7. The process of claim 6 wherein the octane of the desulfurized product is at least 90% that of the feedstock to the olefin-modification reaction zone.

8. The process of claim 1 wherein said feedstock contains basic nitrogen-containing impurities and said process addi-

tionally comprises removing said basic nitrogen-containing impurities from the feedstock before it is contacted with the olefin-modification catalyst.

9. The process of claim 8 wherein said feedstock is comprised of hydrocarbons from a catalytic cracking process.

10. The process of claim 1 wherein said feedstock is substantially free of basic nitrogen-containing impurities.

11. The process of claim 1 wherein said feedstock is comprised of a mixture of hydrocarbons which boils in the gasoline range.

12. The process of claim 1 wherein the feedstock is comprised of a treated naphtha which is prepared by removing basic nitrogen-containing impurities from a naphtha produced by a catalytic cracking process.

13. The process of claim 1 wherein the third fraction ranges from 2 to 10 vol % of the product from the olefin-modification reaction zone.

14. The process of claim 1 wherein the feedstock has an initial boiling point which is below about 79° C. and distillation endpoint which is not greater that about 345° C.

15. A process for producing products of reduced sulfur content from a feedstock, wherein said feedstock contains sulfur-containing organic impurities and is comprised of a normally liquid mixture of hydrocarbons which includes olefins, said process comprising:

(a) contacting the feedstock with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product which has a lower bromine number than that of the feedstock wherein the product contains refractive sulfur compounds, wherein said olefin-modification catalyst is selected from the group consisting of all solid acid catalysts;

(b) fractionating the product from said olefin-modification reaction zone to produce:

(i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 120° C.;

(ii) a second fraction which is higher boiling than the first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 200° C.; and

(iii) a third fraction which is higher boiling than the second fraction and comprises sulfur-containing organic impurities and refractive sulfur compounds;

(c) contacting said second fraction with a selective hydrotreating catalyst in the presence of hydrogen in a selective hydrotreating reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur containing impurities in the second fraction to hydrogen sulfide;

(d) contacting said third fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the third fraction to hydrogen sulfide.

16. The process of claim 15 which additionally comprises removing hydrogen sulfide from the effluent of said selective hydrotreating reaction zone to yield a desulfurized product

having an octane which is at least 98% that of the feedstock to the olefin-modification reaction zone.

17. The process of claim 15 which additionally comprises removing hydrogen sulfide from the effluent of said hydrodesulfurization reaction zone to yield a desulfurized product having an octane which is at least 97% that of the feedstock to the olefin-modification reaction zone.

18. The process of claim 15 wherein said feedstock is comprised of hydrocarbons from a catalytic cracking process.

19. The process of claim 15 wherein the feedstock is comprised of a treated naphtha which is prepared by removing basic nitrogen-containing impurities from a naphtha produced by a catalytic cracking process.

* * * * *

X.

RELATED PROCEEDINGS APPENDIX

NONE